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DIRECT FILTRATION OF LAKE SUPERIOR WATER FOR ASBESTIFORM FIBER REMOVAL. APPENDIX E. ONTARIO RESEARCH FOUNDATION ELECTRON MICROSCOPE ANALYSIS RESULTS. APPENDIX F. EPA NATIONAL WATER QUALITY LABORATORY X-RAY DIFFRACTION ANALYSIS RESULTS. APPENDIX G. UNIVERSITY OF MINNESOTA AT DULUTH ELECTRON MICROSCOPE ANALYSIS RESULTS

Black and Veatch

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June 1975

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16. ABSTRACT

Pilot plant research conducted in 1974 at Duluth, Minnesota, demonstrated that asbestiform fiber counts in Lake Superior water could be effectively reduced by municipal filtration plants. During the study engineering data were also obtained for making cost estimates for construction and operation of both granular and diatomaceous earth (DE) filtration plants ranging in size from 0.03 to 30 mgd. Data provided to the contractor by the Ontario Research Foundation are presented in Appendix E. ORF performed asbestiform fiber analysis of water samples by the transmission electron microscope method in this project. In order to place the data in better perspective, a description of the analytical method used by ORF is reproduced in Appendix E. In Appendix F, the amphibole mass data obtained by the National Water Quality Laboratory in Duluth are presented. This appendix also includes information on the analytical method used at NWQL. The x-ray diffraction analysis for amphibole mass provided confirmation of electron microscope amphibole fiber results. Fiber count data obtained at the University of Minnesota at Duluth are tabulated in Appendix G. A statement describing the electron microscope analytical method is also included.

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DIRECT FILTRATION OF LAKE SUPERIOR WATER FOR ASBESTIFORM FIBER REMOVAL

Appendix E

Ontario Research Foundation Electron Microscope Analysis Results

Appendix F

EPA National Water Quality Laboratory X-Ray Diffraction Analysis Results

Appendix G

University of Minnesota at Duluth Electron Microscope Analysis Results

By

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise, and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment -- air, water and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This report and its appendices present the results of pilot plant filtration research for the removal of asbestiform fibers from drinking water. The several appendices present detailed information on water quality, pilot plant equipment and operation, individual filter run data, asbestiform fiber and amphibole mass concentrations in raw and filtered water, and diatomite filter optimization. Appendix E contains electron microscope analytical results from the Ontario Research Foundation. Appendix F contains x-ray diffraction analytical results from the EPA National Water Quality Laboratory in Duluth. Appendix G contains electron microscope analysis results from the University of Minnesota at Duluth.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

ABSTRACT

Pilot plant research conducted in 1974 at Duluth, Minnesota, demonstrated that asbestiform fiber counts in Lake Superior water could be effectively reduced by municipal filtration plants. During the study, engineering data were also obtained for making cost estimates for construction and operation of both granular and diatomaceous earth (DE) filtration plants ranging in size from 0.03 to 30 mgd.

Data provided to the contractor by the Ontario Research Foundation are presented in Appendix E. ORF performed asbestiform fiber analysis of water samples by the transmission electron microscope method in this project. In order to place the data in better perspective, a description of the analytical method used by ORF is reproduced in Appendix E.

In Appendix F, the amphibole mass data obtained by the National Water Quality Laboratory in Duluth are presented. This appendix also includes information on the analytical methods used at NWQL. The x-ray diffraction analysis for amphibole mass provided confirmation of electron microscope amphibole fiber results.

Fiber count data obtained at the University of Minnesota at Duluth are tabulated in Appendix G. A statement describing the electron microscope analytical method is also included.

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APPENDIX E ONTARIO RESEARCH FOUNDATION ELECTRON MICROSCOPE ANALYSIS RESULTS OF PILOT WATER TREATMENT UNITS - RAW WATER FROM DULUTH LAKEWOOD INTAKE.

Date of sample	Filter utilized	Run No.	f/l x 10^6 Raw sample[c]	f/l x 10^6 Finished sample[c]	Per Cent Removal
4/19	MM-2	1	A=0.304 C=0.217	A=<0.0435 C=0.0435	85 80
4/25	MM-2	7	A=0.348 C=0.174	A=<0.0435 C=0.348	87 --
5/7	BIF	10-T	A=0.522 C=0.130	A=<0.0435 C=1.43	
5/9	BIF	12-T	A=0.870 C=1.78	A=<0.0435 C=<0.0435	
5/16			A=2.61 C=1.35		
5/16	MM-1	7		A=<0.0435 C=0.130	98 90
5/16	MM-2	37		A=<0.0435 C=0.174	98 87
5/16	BIF	8		A=0.565 C=0.652	
5/16	ERD-2	10		A=0.261 C=1.04	90 23
5/30			A=1.43 C=1.83		
5/30	MM-1	26		A=<0.0435 C=0.261	97 86
5/30	MM-2	50		A=<0.0435 C=0.913	96 50
5/30	BIF	17		A=0.739 C=1.83	
5/30	ERD-2	14		A=<0.0435 C=0.0435	97 98
6/4			A=1.74 C=2.91		
6/4	MM-1	29		A=<0.0435 C=0.478	97 83
6/4	MM-2	53		A=<0.0435 C=1.87	97 36
6/4	BIF	19		A=0.217 C=0.0870	
6/4	ERD-2	15		A=0.391 C=1.00	77 66
6/6			A=1.52 C=2.35		
6/6	MM-1	31		A=<0.0435 C=0.348	97 85

APPENDIX E (CONTINUED).

Date of sample	Filter utilized	Run No.	f/l x 10^6 Raw sample[c]	f/l x 10^6 Finished sample[c]	Per Cent Removal
6/6	MM-2	54		A=0.0870	40
				C=0.0870	65
6/6	BIF	20		A=0.0870	
				C=0.739	
6/6	ERD-2	15		A=0.130	91
				C=0.435	82
6/11			A=1.04		
			C=1.65		
6/11	MM-1	34		A=0.174	83
				C=0.174	89
6/11	MM-2	55		A=<0.087	91
				C=2.26	--
6/11	BIF	24		A=0.174	
				C=0.261	
6/11	ERD-1	1A		A=0.957	8
				C=9.31	--
6/13			A=0.48		
			C=0.41		
6/13	MM-1	36		A=<0.0217	96
				C=0.57	--
6/13	MM-2	57		A=0.15	69
				C=2.02	--
6/13	BIF	28		A=0.80	
				C=0.46	
6/13	ERD-1	1A		A=0.09	
				C=0.71	
6/17			A=0.61		
			C=2.15		
6/17	MM-1	39		A=<0.0217	97
				C=0.44	79
6/17	MM-2	61		A=0.04	93
				C=0.37	83
6/17	BIF	31		A=0.09	
				C=0.39	
6/17	ERD-1	4A		A=<0.0217	97
				C=1.37	36
6/24			A=1.04		
			C-3.91		
6/24	MM-1	44		A=<0.0217	80
				C=0.130	97
6/24	MM-2	71		A=0.0217	98
				C=0.978	75
6/24	BIF	37		A=<0.0217	
				C=0.239	

APPENDIX K (CONTINUED).

Date of sample	Filter utilized	Run No.	f/l x 10^6 Raw sample[c]	f/l x 10^6 Finished sample[c]	Per Cent Removal
6/24	ERD-2	22		A=0.0217 C=0.239	
6/28			A=1.11 A=0.91[b] C=8.12 C=3.35[b]		
6/28	MM-1	48		A=<0.0217 C=1.37	98 83
6/28	MM-2	76		A=<0.0217 C=0.52[b]	97 84
6/28	BIF	47		A=0.15 C=6.03	
6/28	ERD-2	28		A=0.11 C=5.3	90 35
7/3			A=0.565 C=3.57		
7/3	MM-1	52		A=<0.0217 C=0.283	96 92
7/3	MM-2	78		A=0.0217 C=0.544	97 86
7/3	BIF	51		A=0.196 C=1.67	
7/3	ERD-2	32		A=0.130 C=0.804	77 77
7/19			A=0.52 C=0.35		
7/19	MM-1	67		A=<0.0217 C=0.15	96 57
7/19	MM-2	96		A=0.02 C=0.04	96 91
7/19	BIF	70		A=<0.0435 C=<0.0435	
7/19	ERD-2	40		A=0.11 C=0.22	79 40
7/23			A=0.54 C=0.09		
7/23	MM-1	70		A=<0.0217 C=0.07	96 22
7/23	MM-2	99		A=<0.0217 C=0.20	96 ---
7/23	BIF	72		A=<0.0217 C=0.76	
7/23	ERD-2	41		A=0.09 C=0.09	83

APPENDIX E (CONTINUED).

Date of sample	Filter utilized	Run No.	f/l x 10^6 Raw sample[c]	f/l x 10^6 Finished sample[c]	Per Cent Removal
7/25			A=0.11 C=1.43		
7/25	MM-1	72		A=<0.0217 C=0.37	82 74
7/25	MM-2	101		A=<0.0217 C=0.15	82 89
7/25	BIF	73		A=0.04 C=0.35	
7/25	ERD-2	43		A=<0.0217 C=0.44	82 69
7/30			A=0.11 C=0.11		
7/30	MM-1	74		A=<0.0217 C=<0.0217	82 82
7/30	MM-2	105		A=<0.0217 C=0.04	82 64
7/30	BIF	77		A=<0.0217 C=0.07	
7/30	ERD-2	45		A=<0.0217 C=0.07	82 36
7/31			A=0.33[b] C=0.22[b]		
7/31	MM-2	106		A=<0.0217 C=<0.0217	94 91
8/1			A=0.22 C=0.15		
8/1	MM-1	76		A=<0.0217 C=0.22	91 --
8/1	MM-2	107		A=0.02 C=<0.0217	91 87
8/1	BIF	79		A=<0.0217 C=0.04	
8/1	ERD-2	46		A=<0.0217 C=0.13	91 13
8/6			A=0.6 C=0.3		
8/6	MM-1	78		A=<0.0217 C=0.06	67 80
8/6	MM-2	109		A=<0.0217 C=<0.0217	97 93
8/6	BIF	82		A=<0.0217 C=0.06	
8/6	ERD-2	48		A=0.02 C=<0.0217	97 93

APPENDIX E (CONTINUED).

Date of sample	Filter utilized	Run No.	f/l x 10^6 Raw sample	f/l x 10^6 Finished sample	Per Cent Removal
8/8			A=0.06 C=0.09		
8/8	MM-1	80		A=0.04 C=0.20	33 --
8/8	MM-2	111		A=<0.0217 C=0.09	67 --
8/8	BIF	84		A=<0.0217 C=0.4	
8/8	ERD-2	49		A=<0.0217 C=0.04	67 55
8/13			A=0.13 C=0.20		
8/13	MM-1	82		A=<0.0217 C=0.03	85 85
8/13	MM-2	113		A=<0.0217 C=1.4	85 --
8/13	BIF	88		A=<0.0217 C=0.1	
8/13	ERD-2	51		A=0.04 C=0.50	69 --
8/15			A=0.09 C=0.17		
8/15	MM-1	84		A=<0.0217 C=0.52	78 --
8/15	MM-2	114		A=0.02 C=0.22	78 --
8/15	BIF	89		A=0.15 C=0.44	
8/15	ERD-2	55		A=0.04 C=0.04	55 76
8/20			A=0.30 C=0.72		
8/20	MM-2	118		A=0.02 C=2.1	93 --
8/20	ERD-2	59		A=<0.0217 C=0.17	93 76
8/22			A=0.13 C=0.37		
8/21	MM-1	86		A=<0.0217 C=0.13	85 65
8/22	MM-1	86		A=<0.0217 C=0.22	85 40
8/22	MM-1	86		A=<0.0217 C=0.80	85 --
8/23			A=0.72 C=0.44		
8/23	MM-2	119		A=<0.0217 C=0.28	97 36

APPENDIX E (CONTINUED).

Date of sample	Filter utilized	Run No.	f/1 x 10^6 Raw sample[c]	f/1 x 10^6 Finished sample[c]	Per Cent Removal
8/23	ERD-2	63		A=0.02	97
				C=0.59	--
8/28			A=0.39		
			C=0.48		
8/28	MM-2	122		A=<0.0217	95
				C=0.04	92
8/28	BIF	103		A=0.15	
				C=0.24	
8/30			A=0.78		
			C=0.33		
8/30	MM-2	124		A=0.02	97
				C=0.30	--
8/30	BIF	105		A=0.04	
				C=0.17	
8/30	ERD-2	68		A=<0.0217	97
				C=0.54	--
9/4			A=1.61		
			C=0.33		
9/4	MM-2	126		A=<0.0217	99
				C=<0.0217	94
9/4	BIF	108		A=0.17	
				C=1.15	
9/4	ERD-2	70		A=<0.0217	99
				C=0.54	--
9/6			A=0.72		
			C=0.39		
9/6	MM-2	128		A=<0.0217	97
				C=0.37	50
9/6	BIF	111		A=0.02	
				C=0.59	
9/6	ERD-2	72		A=<0.0217	97
				C=1.67	--
9/9			A=1.0		
			C=0.5		
9/9	BIF	113		A=0.04	
				C=1.0	
9/9	ERD-2	73		A=<0.0217	98
				C=1.0	--
9/10			A=0.60		
			C=0.50		
9/10	MM-2	131		A=<0.0217	97
				C=0.5	--
9/11			A=0.30		
			C=0.30		
9/11	MM-2	133		A=0.02	93
				C=0.30	--

APPENDIX E (CONTINUED).

Date of sample	Filter utilized	Run No.	f/l x 10^6 Raw sample[c]	f/l x 10^6 Finished sample[c]	Per Cent Removal
9/11	BIF	115		A=<0.0217	93
				C=0.10	67
9/13			A=0.02		
			C=0.06		
9/13	MM-2	137		A=0.02	--
				C=0.10	--
9/13	BIF	117		A=0.02	
				C=0.40	
9/13	ERD-2	78		A=<0.0217	
				C=0.06	
9/16			A=0.90		
			C=0.10		
9/16	MM-2	138		A=0.02	98
				C=0.30	--
9/16	BIF	118		A=<0.0217	
				C=1.30	
9/16	ERD-2	79		A=0.02	98
				C=0.06	40
9/17			A=0.20		
			C=0.10		
9/17	MM-2	139		A=<0.0217	90
				C=0.10	--
9/19			A=0.60		
			C=0.09		
9/19	MM-1	87		A=1.00	--
				C=0.70	--
9/19	MM-2	140		A=<0.0217	97
				C=0.30	--
9/19	BIF	120		A=0.02	
				C=1.80	
9/20			A=1.3		
			C=0.2		
9/20	ERD-2	85		A=0.02	98
				C=0.32	--

[a] BDL - Below detectable limits of analysis equipment

[b] Cloquet Pipeline water

[c] A = amphibole, C = chrysotile

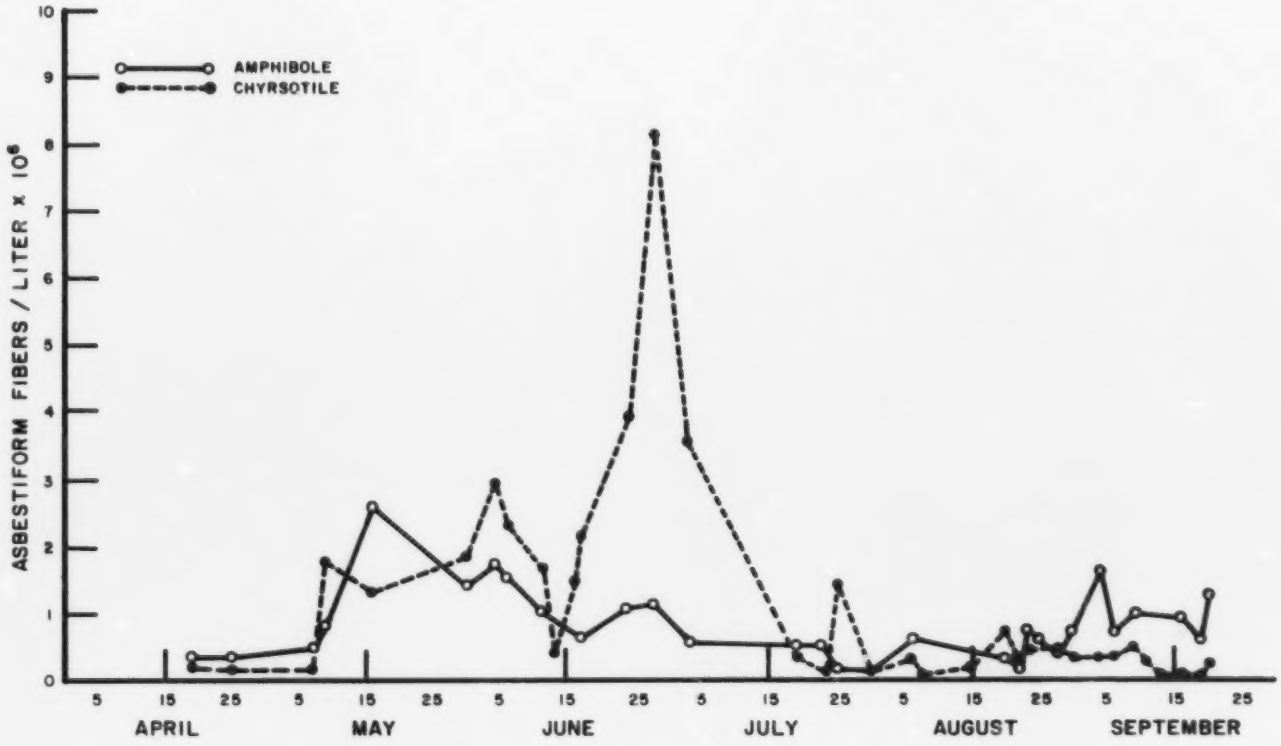

FIGURE 1. ONTARIO RESEARCH FOUNDATION
ASBESTIFORM FIBER COUNTS
RAW WATER AT DULUTH LAKEWOOD INTAKE - 1974

QUANTITATIVE ANALYSIS OF ASBESTOS MINERALS IN AIR AND WATER

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The effects of inhalation of asbestos particles are well known.[1] However, although the significance of asbestos particles when ingested is not fully understood, there is some evidence of increased incidence of gastrointestinal carcinoma where individuals have been exposed to the material over a long period.[2] Methods are therefore required by which trace concentrations of asbestos minerals in both air and ingestibles can be monitored.

Asbestiform minerals fall into two groups, serpentine and amphibole. Chrysotile is the only asbestiform member of the serpentine type, consisting of magnesium silicate $Mg_3Si_2O_5(OH)$. The asbestiform amphiboles have a range of composition $X_7Si_8O_{22}(OH)_2$ where X may be Na, Fe^{2+}, Fe^{3+}, Mg or Ca in various combinations. The principal types of amphibole commonly encountered include crocidolite, anthophyllite, tremolite, and amosite, although amosite itself has a number of sub-species of variable compositions. Although it is commonly thought that asbestos minerals are indestructible, in practice they are decomposed by heat or acids to a variable degree depending on the particular variety. This property restricts the treatment possible in any analytical procedure. This paper describes an analytical technique which is suitable for detection and measurement of low concentrations of asbestiform minerals in air and water samples.

The first step in the procedure is to collect some of the solid material on a 0.1μm pore size membrane filter. In the case of air, about $5m^3$ is filtered; about 200ml in the case of a measurement on water. The membrane filter is then ashed in a clean glass vial using a plasma microincineration technique. The ashing takes place at low temperatures (typically 70°C), thus whilst no decomposition of the mineral fibers can occur, organic materials and the filter itself are oxidised to CO_2. The residue is gently redispersed ultrasonically in filtered distilled water, and the suspension centrifuged on to a 1cm diameter glass cover disc. The disc is dried and a thin carbon coating is applied by evaporation. The carbon film is scored and floated off on to water, carrying the particles with it; pieces of this are then picked up on 200 mesh copper grids. A maximum of 10 grid squares is searched for asbestos particles at a magnification of about 25000. Particles are identified at the instrument by electron diffraction, and measured in both length and width by comparison with a series of geometrically spaced calibration circles scored on the fluorescent screen of the microscope. Typical crocidolite particles are shown in Figure 1, and their single fiber diffraction pattern is shown in Figure 2. Figures 3 and 4 show typical amosite particles and their single fiber diffraction pattern. It can be seen that the diffraction patterns in this case are quite different, although identification within the amphibole series is not generally so simple. In contrast, chrysotile can be easily distinguished by both morphology and its diffraction pattern.

The particle counts are processed by a computer program, which calculates the particle number and mass concentrations; it also plots the number and mass size distributions. Using the sample volumes specified, air concentrations can be measured down to about 0.01 fibers/cc, and water concentrations to 10^4 fibers/liter in typical cases. The actual sensitivity depends on the degree of concentration which can be achieved, whilst retaining a suitable microscope specimen. This in turn is determined by the concentration of extraneous material present in the original sample.

Quantitative Analysis of Asbestos Minerals in Air and Water by E. J. Chatfield is reprinted from 32nd Ann. Proc. Electron Microscopy Soc. Amer., St. Louis, Missouri, 1974, C. J. Arceneaux (ed.), with permission of Claitors Publishing Division, 3165 South Arcadin, Baton Rouge, La.

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**32nd Ann. Proc. Electron Microscopy Soc. Amer."
St. Louis, Missouri, 1974. C. J. Arceneaux (ed.).**

An extensive study has been made of water samples in Ontario,[3] following a small pilot study by a different technique,[4] The water in Ontario generally contains an average of about 2 million fibers of chrysotile per liter, and usually no detectable amphibole types.

1. I. J. Selikoff et al, Arch. Environ. Health, 25, p. 1-13, (1972).
2. T. F. Mancuso and E. J. Coulter, Arch. Environ. Health, 6, p. 210, (1963).
3. G. Kay, Water and Pollution Control, Sept. 1973, p. 33-35.
4. J. M. Cunningham and R. Pontefract, Nature, 232, p. 332, (1971).

Figure 1. Crocidolite Fibers

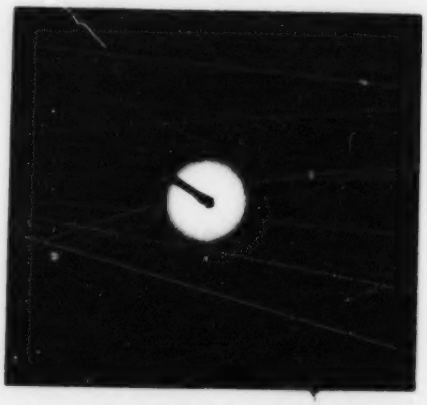

Figure 2. Crocidolite Single Fiber Diffraction Pattern

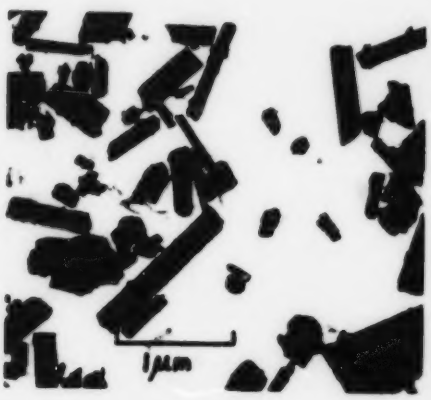

Figure 3. Amosite Fibers

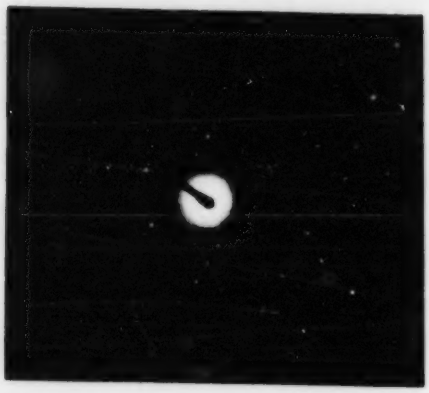

Figure 4. Amosite Single Fiber Diffraction Pattern

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Measuring asbestos in the environment

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THE INCIDENCE of asbestos-related disease reported by medical authorities and its classification as a hazardous material [1-10] has created a need for techniques by which it can be measured at low concentrations in air and water samples.

To appreciate the criteria involved in the design of such low level analytical methods, it is useful to review some of the recent history of asbestos-related disease, the established maximum occupational exposure levels, and the properties of the materials themselves. Until recently, inhalation was considered to be the only hazard associated with this material, and fairly reliable data are available relating the incidence of the progressive disease asbestosis with the individual's exposure. Indeed, occupational exposure levels have been defined for some years in both the USA and Britain. However, in the last few years a previously rare malignancy condition, mesothelioma, has been linked with exposure to asbestos, this exposure not always being an occupational one. [11] Furthermore, statistical studies have shown that persons exposed to asbestos minerals show a greater incidence of various types of gastrointestinal carcinoma. [12-14] As a consequence, public health authorities in most civilized countries are re-assessing the significance of the presence of asbestos minerals in the environment. The discovery that many Canadian water supplies contain upwards of 1 million asbestos fibres per litre [12,13] has also given cause for surveys of municipal water sources to be made, whilst in the United States, disposal of mine tailings in Lake Superior in the vicinity of Duluth, Minnesota has led to an extended Federal court action [15] against the company involved. These recent events indicate the seriousness with which the authorities now view the natural presence of, or the discharge of, this material into the environment, and it appears to be only a matter of time before some guidelines are established concerning acceptable levels in both air and water for the general population. [16] On the other hand, the importance of asbestos in most sectors of the economy cannot be denied.

As previously mentioned, occupational levels for workers in the asbestos industry have existed for some time; however, there appears to be a considerable divergence of opinion on just how these levels should be established. The recommended North American occupational MPC (Maximum Permissible Concentration) for air has been set at 5 fibres/ml; [17] a further condition is that only those fibres greater than 5 μm in length are included in this figure. At the time of writing there is no MPC for ingestibles. The occupational MPC in the UK has been set at 2 fibres/ml, [18,19] with the same fibre length limitation. In this case, some discrimination between the various asbestos mineral types is exercised, and mass concentration values are also equated to these for convenience of measurement. It must be emphasized that these are all OCCUPATIONAL levels which are established using statistical data and by defining some small incidence of asbestos-related disease in the industry as acceptable. If the normal philosophy used in radiation protection were to be applied, acceptable levels for exposure of the general population would logically be set at substantially lower values, perhaps one order of magnitude or so lower. The design of a suitable measurement technique for asbestos minerals must therefore take account of the low levels to be measured. For air, a suitable lower detection limit appears to be about 0.01 fibres/ml, whilst for water the corresponding value would be about 10^6 fibres/litre, this latter figure being about 100 times less than the average concentrations normally found.

Asbestos is a generic term used for two families of minerals which have a fibruous texture and which can be split into individual, sometimes very flexible fibres. The first group are the serpentines, of which chrysotile is the only fibrous member. This mineral comprises most of the world's production, and nearly all of the Canadian contribution to it. It is a hydrated magnesium silicate, having the composition $Mg_3Si_2O_5(OH)_4$, and is not the "indestructible" material it is commonly thought to be. It is attacked by even the weak acids, such as acetic acid, and decomposes on heating at 450C to Forsterite, which is not fibrous, although it may still retain the fibrous morphology of the parent material. Individual fibres of chrysotile have been observed to decompose at temperatures as low as 250C. [20] The other group of fibrous minerals are the amphiboles, which have the general composition $X_7Si_8O_{22}(OH)_2$, where X may be $Na^{\oplus}$, Fe^{++}, Fe^{+++}, Mg^{++}, or Ca^{++} in various combinations. [20] These minerals possess greater resistance to acids and heat than chrysotile, and a number of specific compositions are recognized and named as individual minerals. The principal types thus recognized are amosite, grunerite, anthophyllite, crocidolite, actinolite and tremolite. The amosite-grunerite series has a variable composition which has led to the naming of a number of other sub-species such as Cummingtonite, the mineral involved in the western arm of Lake Superior.

From the compositions given above, it can be seen that many other mineral species may have similar compositions, yet not be asbestiform types. The only identification technique open to us, therefore, is one sensitive to the crystal structure, i.e. either electron or X-ray diffraction. Chemical analysis by itself is not useful. In some cases, only a combination of the two is adequate. Since most of the health criteria are stated in terms of fibre **number** concentrations, all mass measurement techniques, including X-ray diffraction, are excluded. In any case, X-ray diffraction is of marginal sensitivity, particularly when other common minerals such as kaolinite are also present. [20] Along with most other in-

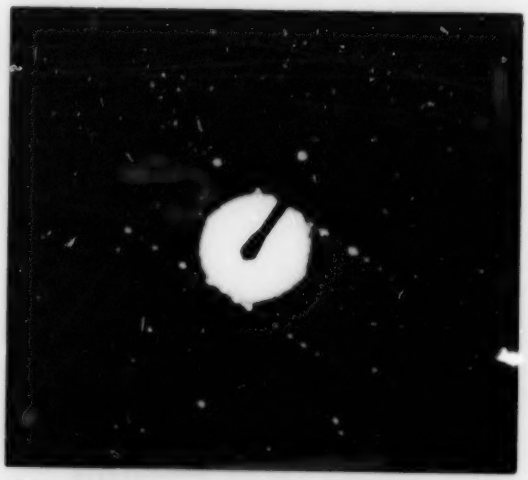

Figure 6–Electron diffraction pattern of amosite

Figure 5–Electron micrograph of amosite X5,000

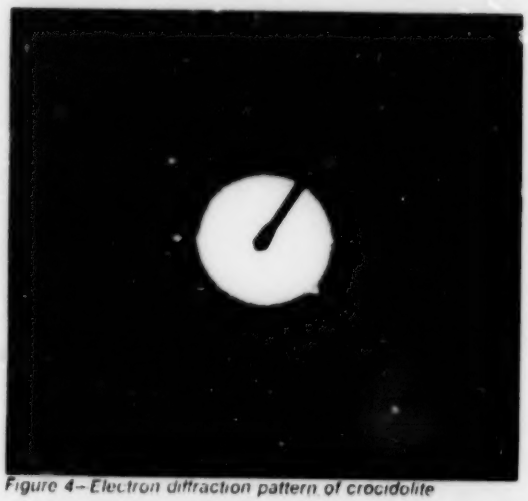

Figure 4–Electron diffraction pattern of crocidolite

Figure 3–Electron micrograph of crocidolite X23,000

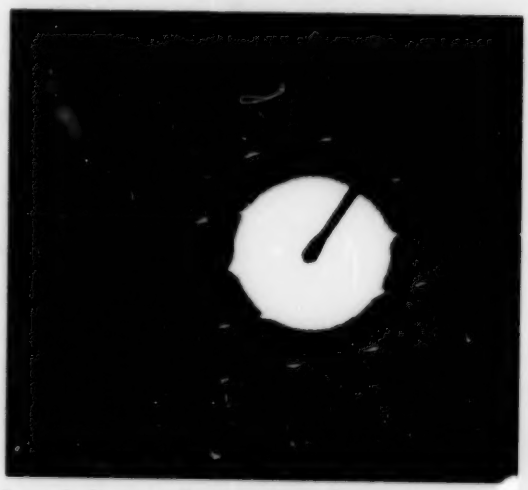

Figure 2–Electron diffraction pattern of chrysotile asbestos

Figure 1–Electron micrograph of chrysotile asbestos X84,000

vestigators, we elected for the only obvious approach: particle counting by electron microscopy, combined with electron diffraction for identification.[11, 12, 13] Although scanning electron microscopy has also been suggested as a suitable alternative, it is evident that identification can only be based on morphology, with perhaps some chemical data from energy dispersive X-ray analysis. Optical microscopy, using techniques such as that currently used for health control in the industry, is also inapplicable to trace measurement in environmental samples, since this technique assumes all fibrous material to be asbestos and lacks any easy identification technique for small particles. It is also found that many fibres have widths much lower than those capable of being resolved by the optical microscope, even though their lengths may exceed the 5 μm length limit sometimes specified.

The whole topic of trace asbestos measurement is surrounded by controversy, and the area subject to most dispute is undoubtedly that of specimen preparation. The requirement of the preparation technique is to quantitatively deposit the solid content of an air or water sample onto an electron microscope specimen support film. It would be desirable to use the technique of Kalmus,[27] in which direct dissolution of the membrane filter is achieved by reflux washing in acetone vapour, thus depositing the particulate material quantitatively on a carbon coated electron microscope grid. This technique suffers from the disadvantage that some smaller particles are washed away; a fact that can easily be checked by processing a radioactive particulate sample. More significantly, raw water samples often contain an overwhelming proportion of organic material, which necessitates dilution of the sample so that a reasonably loaded electron microscope sample can be obtained. This dilution has the undesirable effect of separating the asbestos fibres more widely, thus requiring more counting time. Also the large amount of extraneous organic material obscures many of the fibres. It is therefore preferable to contrate the asbestos fibres at the expense of the organic materials present.

The technique developed for analysis of water samples at ORF is a modification of those described by Cunningham and Pontefract,[14] and Biles and Emerson.[28] At this time it represents the only published technique which has been tested for mass balance using standard asbestos dispersions. Even this has only been tested in the case of chrysotile. The same method is also used for air samples collected on membrane filters.

The first step in the procedure is to collect some of the solid material on a filter. In the case of air, the collection properties of membrane filters allow pore sizes of 0.4 μm or even 0.8 μm to be used, and a volume of about 5m³ is filtered. For water samples, the particle sizes collected are strictly a function of pore size, and the smallest pore size compatible with a reasonable flow-rate is selected. In practice 0.1 μm is the smallest convenient pore size, and a volume of about 200ml of the water is filtered. The remaining steps in the alaytical procedure for both types of sample are identical. The filter is transferred to a clean glass vial, which is then placed in a plasma micro-incinerator (low temperature asher). In this device the filter is oxidized, along with all other organic materials present, with very little disturbance at a temperature of less than 80C°. The oxidation takes place in oxygen at a pressure of about 1 Torr, which is excited by a radio-frequency discharge. After some hours the vial containing the residue is removed and double distilled water added. The ashed residues are gently dispersed ultrasonically and an aliquot of the dispersion is centrifuged on to a 1cm diameter cover glass at an acceleration of 8,000g for about 20 minutes. In practice, a drop of very dilute detergent is also added to the centrifuge tube for a reason which is referred to later. The disc is removed, dried and a thin carbon coating applied by vacuum evaporation. The carbon film is scored by a scalpel blade, and is then floated on to water, carrying the deposit of particles with it. The detergent which was added to the centrifuge tube assists in the removal of the carbon film from the glass disc. Pieces of the carbon are then picked up on 200 mesh electron microscope support grids.

About 10 grid squares, selected from several grids, are searched for asbestos particles using a trans-

ASBESTOS FIBRE COUNT ANALYSIS

DATE: 15/12/73

SIZE CATEGORY	PARTICLE SIZE, UM	NUMBER COUNTED	CUM NUMBER	CUM NO PERCENT	CUM MASS PERCENT
1	0.040	0	0.0	0.00	0.00
2	0.057	0	0.0	0.00	0.00
3	0.080	0	0.0	0.00	0.00
4	0.113	1	0.5	0.56	0.09
5	0.160	20	11.0	12.36	2.86
6	0.226	16	29.0	32.58	8.94
7	0.320	16	45.0	50.56	16.88
8	0.453	16	61.0	68.54	27.47
9	0.640	8	73.0	82.02	38.87
10	0.905	7	80.5	90.45	49.50
11	1.280	2	85.0	95.51	58.08
12	1.810	1	86.5	97.19	64.23
13	2.560	1	87.5	98.31	71.53
14	3.620	0	88.0	98.88	75.81
15	5.120	0	88.0	98.88	75.81
16	7.241	1	88.5	99.44	87.90
17	10.240	0	89.0	100.00	100.00

TOTAL NUMBER OF PARTICLES COUNTED = 89
SIZE OF GRID SQUARE USED = 85 MICROMETRES
NUMBER OF GRID SQUARES COUNTED = 10
DENSITY USED IN MASS CALCULATION = 2.40 G/CC

TYPE OF ASBESTIFORM COUNTED - CHRYSOTILE

CONCENTRATION OF ASBESTOS = 1.93×10^{6} FIBRES/LITRE

ESTIMATED MASS CONCENTRATION = 3.93×10^{-3} MICROGRAMS/LITRE

I.E. ONE PART OF ASBESTOS IN 2.55×10^{11} PARTS OF LIQUID

LOWEST DETECTABLE LEVELS UNDER THE CONDITIONS USED IN THESE MEASUREMENTS

NUMBER - 2.17×10^{4} FIBRES/LITRE

MASS - 7.42×10^{-6} MICROGRAMS/LITRE

Figure 7—Computer printout for a chrysotile-in-water sample

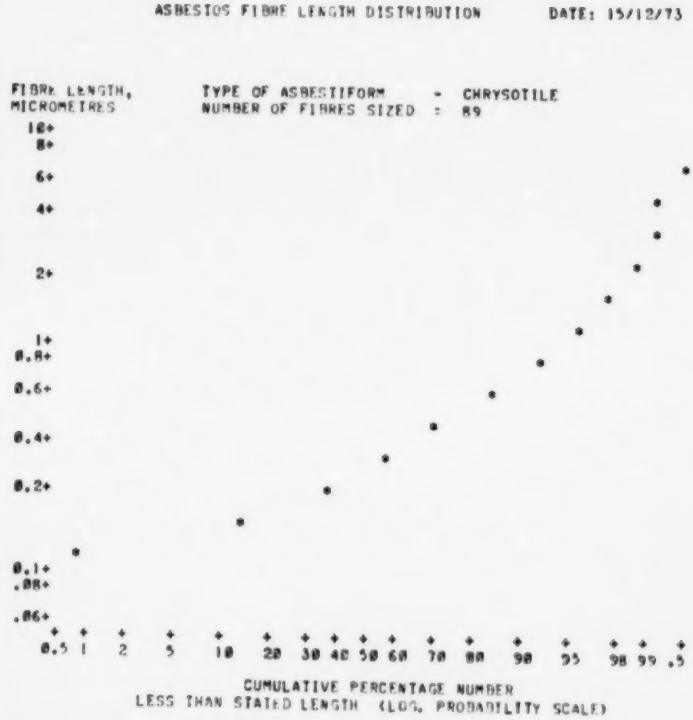

Figure 8—Fibre length distribution of a typical sample

Figure 9—Removing a set of samples from the asher

mission electron microscope at a magnification of approximately 25,000. Asbestiform particles are identified individually by electron diffraction, and their lengths and widths are measured.

The particle counting is normally terminated after 10 grid squares have been examined, or when about 100 particles have been counted. Both the detection level and the accuracy can be improved by additional counting, but for economic reasons these arbitrary limits have usually been applied. The minimum level, i.e. one particle detected, corresponds to about 10^5 particles/litre for water samples, or 0.01 particles/ml for air samples, whilst detection of about 100 particles yields an accuracy of 10%.

The data are then processed by a computer program, which calculates both number and mass concentrations, and also plots the size distributions.

It is the practice of some workers to identify only a minor proportion of the asbestos particles by diffraction. Although chrysotile may be identified primarily by its characteristic morphology in the transmission electron image, the amphiboles possess no such characteristic appearance. In water samples, particularly, diatomaceous and mica fragments can often be mistaken for amphibole fibres. It proves little to identify only 15% of the reported fibres by diffraction, and the OKI alaytical team report only those amphibole fibres which have been so confirmed.

The technique has been criticized for its use of ultrasonics to redisperse the sample residues after the ashing procedure. The concern is that the ultrasonic treatment may break up the fibres, giving rise to an artificially high measurement. In fact, it can be shown that power densities of some watts/ml are required before significant breakage of suspended particles occurs, whereas the power densities used in this technique are only a few milliwatts/ml. However, although we do not regard this as a cause for concern, there are many unresolved questions. For example, water samples have to be collected in the field, and these are usually stored in bottles during transit to the laboratory. Nothing is known about the scavenging action of the bottle's interior surfaces on the suspended particles during storage, the effect of pH, or whether plastic or glass bottles should be used on this account. This effect may also be dependent on particle concentration. The only reliable procedure may be that of immediate

filtration. The mass balance in many of the analytical methods in use is also suspect, and may indicate that results being obtained are lower than the real values.

Contamination is a very serious problem: almost all reagents, glassware, water, etc., are contaminated in some degree with chrysotile asbestos, and the most extreme precautions must be taken to eliminate this. Even some membrane filters have been found to contain amounts of chrysotile which can disrupt the measurement. At ORF we perform critical phases of sample preparation in a positive pressure clean room, from which all known sources of asbestos have been excluded. The air supply is filtered and passed through an electrostatic precipitator. The floor is of pure vinyl, rather than vinyl-asbestos, and a suspended ceiling was fitted to prevent possible fallout from insulated air ducts and pipes. To minimize the dust problem, steel furniture was installed rather than the wood variety. Any visible dust is treated with suspicion and cleaned up using wet tissues to prevent its dispersal. Disposable laboratory coats and overshoes are used by all personnel entering this area. Glassware is cleaned before use in chromic acid, and then rinsed in double distilled water. Only by observing the strictest hygiene, comparable with that necessary during handling of radioactive isotopes, is it possible to maintain the low background measurements which we routinely achieve. Even use of some types of talcum powder or cosmetics by the individuals performing sample preparation can cause a perplexing series of contaminated samples to arise where blank measurements were expected.

The techniques in use at ORF for trace asbestos measurement have been developed over a period of three years. During that time many of the difficulties have been identified and solutions found. However, there is a pressing need for further development work, particularly in the field of quantitative sample preparation. A development program is therefore being initiated at ORF to investigate the various aspects of sample preparation and storage, with the eventual aim of defining a recommended analytical procedure which has been thoroughly tested. Until this program is completed, the current method, which gives reasonably reliable data at an economically acceptable cost, will remain in use.

References

1 Selikoff, I. F. et al. Arch. Environ. Health, Vol. 25, 1972, page 1.

2 Mancuso, T. F. and Coulter, E. F. Arch. Environ. Health, Vol. 6, 1963, page 230.

3 Howitt, D. G. Ann. NY Acad. Sci., 132, 1965, page 64.

4 Wagner, J. C. Ann. NY Acad. Sci., 132, 1965, page 575.

5 Knox, J. F. et al. Brit. J. Indust. Med., 25, 1968, page 293.

6 Newhouse, M. L. and Wagner, J. C. Brit. J. Indust. Med., 26, 1969, page 302.

7 Keal, E. E. Lancet, ii, 1960, page 1211.

8 Hinson, K. F. W. Brit. J. Dis. Chest, 59, 1965, page 125.

9 Federal Register (U.S.A.), Vol. 37, No. 110, 1972, page 11318.

10 Statutory Instruments (U.K.), 1969, No. 690, Factories, The Asbestos Regulations.

11 Newhouse, M. L. and Thompson, H. Brit. J. Indust. Med., 22, 1965, page 261.

12 Cunningham, H. M. and Pontefract, R. Nature, 232, 1971, page 332.

13 Kaas, G. H. Journal AWWA, Sept. 1974, page 513, and Water and Pollution Control, Sept. 1973, page 33.

14 USA vs Reserve Mining Company, 1973-1974.

15 Brackman, L. and Rubino, R. A. "National Behind a Proposed Asbestos Air Quality Standard". 67th Meeting of Air Pollution Control Association, Denver, Col., 1974.

16 Auer, H. E. et al. Ann. NY Acad. Sciences, 132, Art. 1, 1965, page 274.

17 Brit. Occ. Health Soc. Report of Committee on Hygiene Standards - Hygiene Standards for Chrysotile Asbestos Dust, Dec. 1967.

18 Berry, F. Private Communication.

19 Industrial Minerals and Rocks, Ed. J. T. Gibson, AIME, page 46, (1968).

20 Rickards, A. L. and Rubatto, D. V. Nature, 234, 1971, page 93.

21 Smith, G. R. et al. Proceedings Electron Microscopy Society of America, 1973, page 380.

22 Walker, C. W. et al. Proceedings Electron Microscopy Society of America, 1974, page 574.

23 Medlock, G. and Kramer, J. R. Ibid, page 526.

24 Chatfield, C. J. Ibid, page 524.

25 Chatfield, C. J. Proceedings Microscopical Society of Canada, 1974, page 24.

26 Riley, R. and Emerson, T. R. Nature, 229, 1968, page 95.

27 Kaimins, E. H. J. Appl. Phys., 35, (1964).

28 Thomas, R. S. and Cowell, M. J. Proceedings Electron Microscopy Society of America, 1973, page 154.

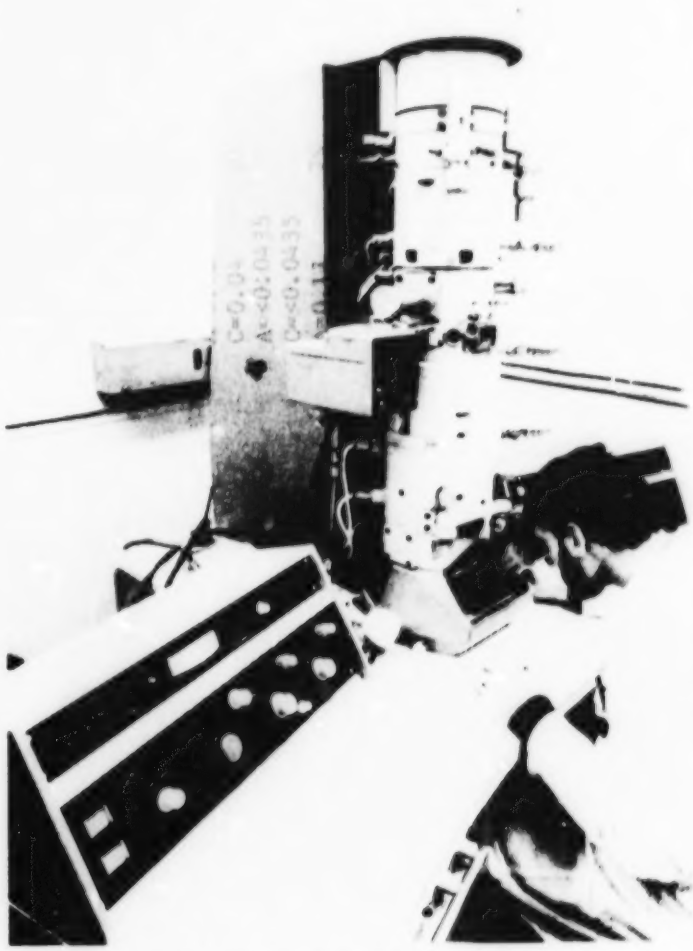

Figure 10—Identifying an asbestos fibre in the transmission electron microscope

APPENDIX F EPA NATIONAL WATER QUALITY LABORATORY X-RAY DIFFRACTION ANALYSIS RESULTS OF PILOT WATER TREATMENT UNITS - RAW WATER FROM DULUTH LAKEWOOD INTAKE.

Date of sample	Filter utilized	Run No.	SS (mg/l)		Amphibole mass concentration (mg/l)		Per Cent Removal
			Raw	Finished	Raw	Finished	
4/19	MM-2	1	0.90	0.43	0.10	<0.02	80
4/25	MM-2	7	0.86	0.39	0.12	<0.02	83
5/7	BIF	10-T	0.69	0.09	0.06	<0.01	83
5/9	BIF	12-T	0.61	0.31	0.22	0.003	98
5/16			0.64		0.14		
5/16	MM-1	7		0.13		0.005	96
5/16	MM-2	37		0.05		0.003	98
5/16	BIF	8		0.12		0.006	96
5/16	ERD-2	10		0.05		0.003	98
5/22			0.74		0.20		
5/22	MM-1	16		0.33		<0.01	95
5/22	MM-2	43		0.13		<0.003	98
5/22	BIF	11		2.63[a]		<0.03	
5/22	ERD-2	13		0.04		0.002	99
5/30			0.68		0.19		
5/30	MM-1	26		0.10		<0.01	95
5/30	MM-2	50		0.05		0.005	97
5/30	BIF	17		1.02[a]		<0.02	
5/30	ERD-2	14		0.10		0.004	98
6/4			0.57		0.26		
6/4	MM-1	29		0.09		<0.006	98
6/4	MM-2	53		0.02		<0.006	98
6/4	BIF	19		0.11		0.004	
6/4	ERD-2	15		0.10		0.003	99
6/6			0.77		0.18		
6/6	MM-1	31		0.12		<0.005	97
6/6	MM-2	54		0.04		<0.005	97
6/6	BIF	20		0.17		0.004	
6/6	ERD-2	15		0.36[a]		<0.004	98
6/11			1.30		0.18		
6/11	MM-1	34		0.24		0.006	97
6/11	MM-2	55		0.07		<0.004	98
6/11	BIF	24		0.59[a]		0.008	
6/11	ERD-1	1A		1.47		<0.02	89
6/17			0.86		0.17		
6/17	MM-1	39		0.12		<0.006	96
6/17	MM-2	61		0.08		<0.01	94
6/17	BIF	31		3.22[a]		<0.03	
6/17	ERD-1	4A		0.06		<0.005	97
6/28			0.74		0.16		
6/28			2.09[b]		0.11[b]		

APPENDIX F (CONTINUED).

Date of sample	Filter utilized	Run No.	SS (mg/l) Raw	SS (mg/l) Finished	Amphibole mass concentration (mg/l) Raw	Amphibole mass concentration (mg/l) Finished	Per Cent Removal
6/28	MM-1	48		0.76		0.007	97
6/28	MM-2	76		0.04[b]		<0.005[b]	95
6/28	BIF	47		0.38		<0.008	
6/28	ERD-2	28		0.68		<0.01	91
7/3			0.75		0.07		
7/3	MM-1	52		0.11		<0.004	95
7/3	MM-2	78		0.08		<0.003	96
7/3	BIF	51		0.65[a]		<0.004	
7/3	ERD-2	32		0.12		0.003	96
7/19			0.88		0.13		
7/19	MM-1	67		0.10		<0.003	98
7/19	MM-2	96		0.18		<0.005	96
7/19	BIF	70		0.60[a]		<0.003	
7/19	ERD-2	40		0.04		<0.003	98
7/23			0.59		0.09		
7/23	MM-1	70		0.03		<0.003	97
7/23	MM-2	99		0.08		<0.004	95
7/23	BIF	72		0.70[a]		0.007	
7/23	ERD-2	41		0.06		<0.003	97
7/25			0.68		0.04		
7/25	MM-1	72		0.08		<0.005	87
7/25	MM-2	101		0.10		<0.005	87
7/25	BIF	73		0.45[a]		<0.004	
7/25	ERD-2	43		0.03		<0.003	92
7/30			0.68		0.10		
7/30	MM-2	104		0.78[c]		0.02	80
7/30			0.64		0.06		
7/30	MM-1	74		0.03		<0.003	95
7/30	MM-2	105		0.14		<0.005	92
7/30	BIF	77		0.13		<0.003	
7/30	ERD-2	45		0.04		<0.003	95
7/31			2.58[b]		0.10[b]		
7/31	MM-2	106		0.09[b]		<0.003[b]	97
8/1			0.90		0.08		
8/1	MM-1	76		0.06		<0.004	95
8/1	MM-2	107		0.06		<0.003	96
8/1	BIF	79		0.24[a]		0.01	
8/1	ERD-2	46		0.06		<0.002	97
8/6			0.70		0.09		
8/6	MM-1	78		0.03		<0.003	97
8/6	MM-2	109		0.06		<0.003	97
8/6	BIF	82		0.71[a]		<0.007	
8/6	ERD-2	48		0.03		<0.002	98
8/8			0.64		0.05		
8/8	MM-1	80		0.06		<0.003	94
8/8	MM-2	111		0.10		<0.003	94

APPENDIX F (CONTINUED).

Date of sample	Filter utilized	Run No.	SS (mg/1) Raw	SS (mg/1) Finished	Amphibole mass concentration (mg/1) Raw	Amphibole mass concentration (mg/1) Finished	Per Cent Removal
8/8	BIF	84		0.59[a]		<0.006	
8/8	ERD-2	49		0.04		<0.002	96
8/13			0.67		0.06		
8/13	MM-1	82		0.03		<0.003	95
8/13	MM-2	113		0.04		<0.003	95
8/13	BIF	88		0.47[a]		<0.005	
8/13	ERD-2	51		0.09		<0.003	95
8/15			0.81		0.06		
8/15	MM-1	84		0.08		<0.003	95
8/15	MM-2	114		0.05		<0.003	95
8/15	BIF	89		0.25		<0.003	
8/15	ERD-2	55		0.16		<0.003	95
8/20			0.81		0.02		
8/20	MM-2	118		0.09		<0.003	85
8/20	ERD-2	59		0.04		<0.003	85
8/21	MM-1	86		0.05		<0.003	85
8/22			0.70		0.03		
8/22	MM-1	86		0.06		<0.003	90
8/22	MM-1	86		0.06		<0.003	90
8/23			0.63		0.04		
8/23	MM-2	119		0.02		<0.003	92
8/23	ERD-2	63		0.05		<0.003	92
8/28			0.54		0.09		
8/28	MM-2	122		0.02		<0.003	97
8/28	BIF	103		0.14		<0.003	
8/30			0.41		0.07		
8/30	MM-2	124		0.03		<0.003	96
8/30	BIF	105		0.27[a]		<0.003	
8/30	ERD-2	68		0.008		<0.003	97
9/4			0.72		0.10		
9/4	MM-2	126		0.03		<0.003	97
9/4	BIF	108		0.55[a]		<0.006	
9/4	ERD-2	70		0.03		<0.003	97
9/6			0.61		0.07		
9/6	MM-2	128		0.04		<0.003	96
9/6	BIF	111		0.38[a]		<0.003	
9/6	ERD-2	72		0.01		<0.003	96
9/9			0.60		0.04		
9/9	BIF	113		0.10		<0.003	
9/9	ERD-2	73		0.03		<0.003	92
9/10			0.62		0.05		
9/10	MM-2	131		0.08		<0.003	94

APPENDIX F (CONTINUED).

Date of sample	Filter utilized	Run No.	SS (mg/l) Raw	SS (mg/l) Finished	Amphibole mass concentration (mg/l) Raw	Amphibole mass concentration (mg/l) Finished	Per Cent Removal
9/11			0.63		0.06		
9/11	MM-2	133		0.08		<0.003	95
9/11	BIF	115		0.52[a]		<0.005	
9/13			0.51		0.09		
9/13	MM-2	137		0.03		<0.003	97
9/13	BIF	117		0.25		<0.003	
9/13	ERD-2	78		0.02		<0.003	97
9/16			0.31		0.08		
9/16	MM-2	138		0.04		<0.003	96
9/16	BIF	118		0.39[a]		<0.004	
9/16	ERD-2	79		0.04		<0.003	96
9/17			0.58		0.06		
9/17	MM-2	139		0.07		<0.003	95
9/19			0.50		0.10		
9/19	MM-1	87		0.06		<0.003	97
9/19	MM-2	140		0.03		0.003	97
9/19	BIF	120		0.40[a]		<0.004	
9/20			0.40		0.07		
9/20	ERD-2	85		0.003		<0.003	96

[a] Mostly DE
[b] Cloquet Pipeline water
[c] Mostly alum and DE, sample purposely collected after turbidity breakthrough

At the concentrations of fibers encountered in Lake Superior water, there appeared to be no correlation between turbidity and fiber counts for either amphibole or chrysotile fibers. However, there was a relationship between raw water amphibole mass and amphibole fiber counts, as shown in Figure 1. Using linear regression analysis, the following was obtained:

$$F/1 = (0.15 + 6.2 \text{ Mass}) \times 10^6$$

F/1 = amphibole fiber count, 10^6 f/1

Mass = amphibole mass, mg/1

The correlation coefficient, r, was 0.48.

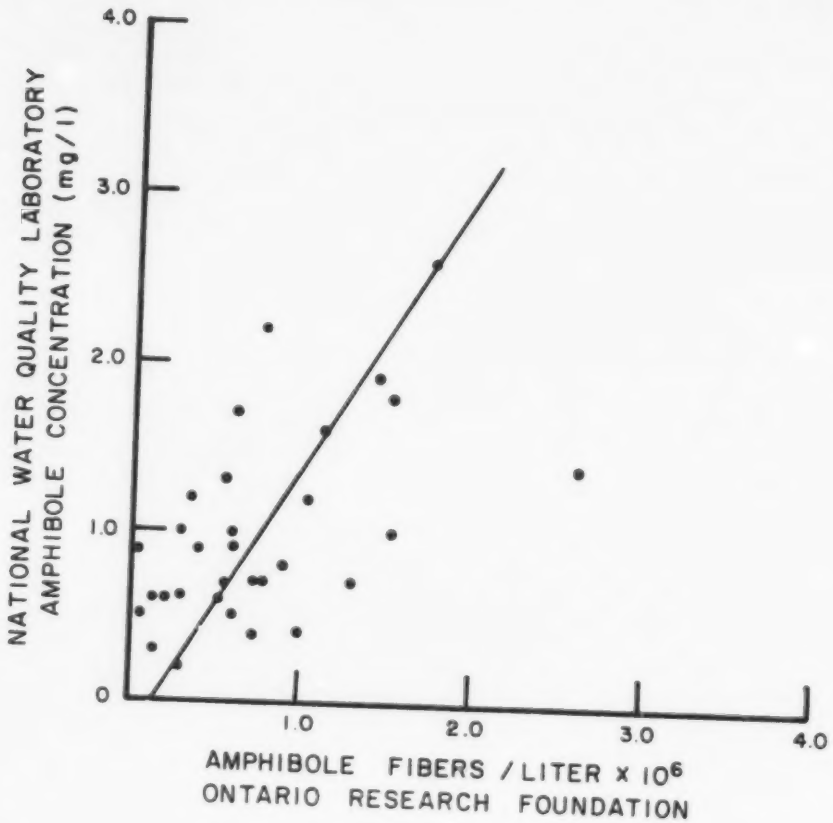

FIGURE 1. CORRELATION BETWEEN NWQL AMPHIBOLE MASS CONCENTRATION AND ORF AMPHIBOLE FIBER COUNTS - RAW WATER AT DULUTH LAKEWOOD INTAKE - 1974

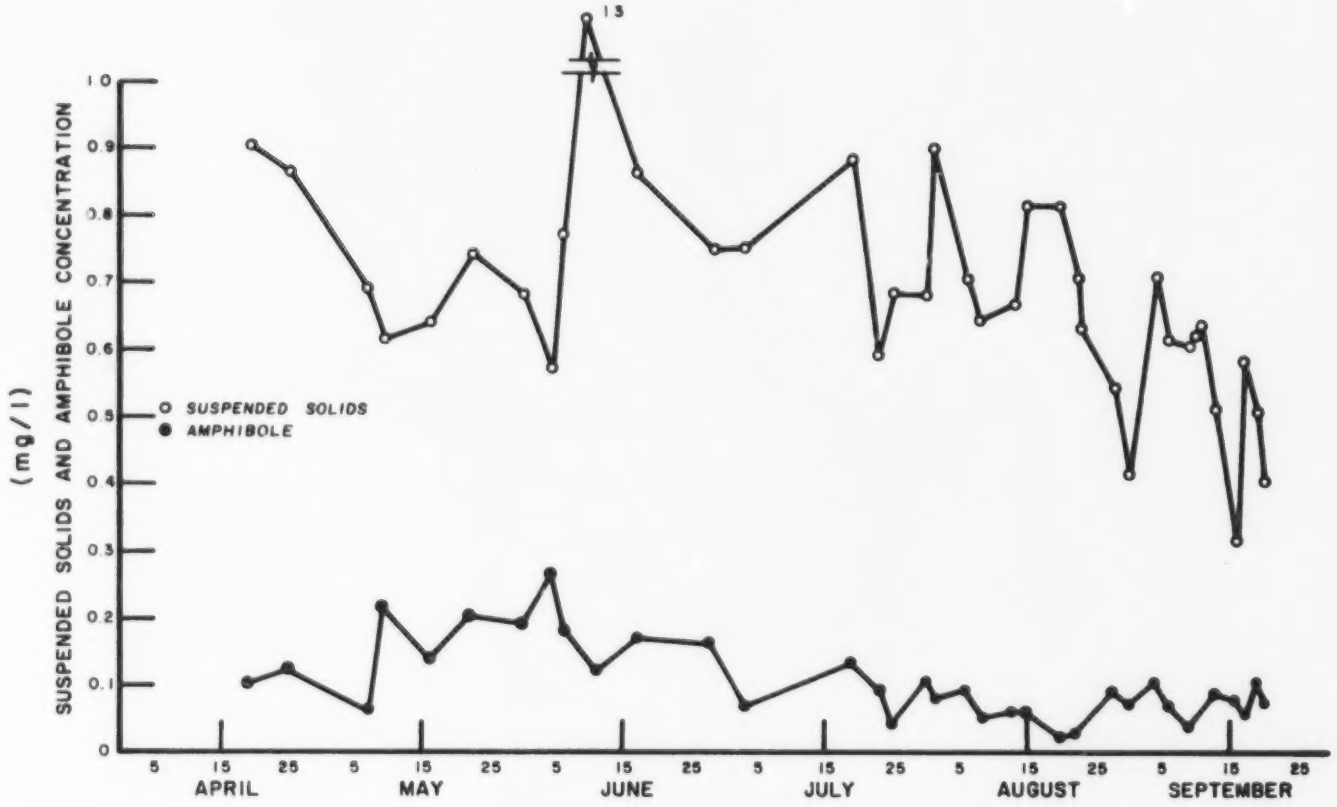

FIGURE 2. ENVIROMENTAL PROTECTION AGENCY
NATIONAL WATER QUALITY LABORATORY
SUSPENDED SOLIDS AND AMPHIBOLE MASS CONCENTRATION
RAW WATER AT DULUTH LAKEWOOD INTAKE - 1974

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SEMI-QUANTITATIVE DETERMINATION OF ASBESTIFORM AMPHIBOLE MINERAL CONCENTRATIONS IN WESTERN LAKE SUPERIOR WATER SAMPLES

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ABSTRACT

The amphibole mineral, cummingtonite-grunerite, has been used as a tracer for taconite tailings discharged into Western Lake Superior. The discovery of many asbestiform amphibole fibers in the tailings and Western Lake Superior water lead to concern over fiber concentrations in municipal water supplies using this water. This concern was based on the association between human asbestos exposure and increased rates of cancer of the gastrointestinal tract and peritoneum. An x-ray diffraction external standard technique has been developed for rapid, inexpensive, semi-quantitative determinations of amphibole mass concentration in water. The average amphibole mass concentrations for different Western Lake Superior water intakes compare very well with the average electron microscope fiber counts for the same samples. Daily amphibole analysis of the Duluth water supply indicates an average amphibole concentration of 0.19 milligrams per liter.

INTRODUCTION

For several years x-ray diffractometry has been the key analytical technique for National Water Quality Laboratory studies of the distribution and fate of taconite tailings which have been discharged into Western Lake Superior at Silver Bay, Minnesota since 1956. A major component of this 67,000 ton per day discharge, the amphibole mineral cummingtonite-grunerite, provides an ideal tracer for the tailings. The cummingtonite-grunerite (310) peak at 29.1° 2θ for copper K_α radiation (d = 3.07 Å) is not found in x-ray diffraction patterns for natural lake sediments or suspended

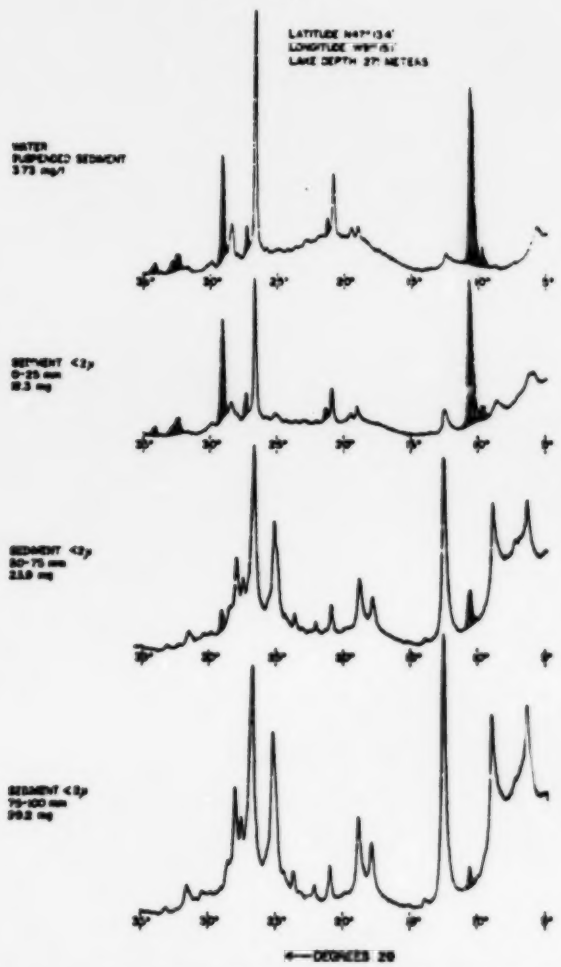

FIGURE 1---X-RAY DIFFRACTION PATTERNS (COPPER RADIATION) FROM SEDIMENT SAMPLES TAKEN AT SUCCESSIVE 25 MM INTERVALS IN AN AREA OF TACONITE TAILINGS DEPOSITION. CUMMINGTONITE-GRUNERITE, $(Mg,Fe)_7Si_8O_{22}(OH)_2$, PEAKS ARE SHADED. THE (110) PEAK AT APPROXIMATELY 10.6° 2θ IS COMMON TO MOST AMPHIBOLES

solids. X-ray diffraction patterns (Figure 1) of lake water suspended solids which contain taconite tailings and sediment from successive 25 mm sections of the lake bottom in an area of tailings deposition show a clear gradation from large amounts of cummingtonite-grunerite (shaded peaks) in very recent surficial sediments to no cummingtonite-grunerite and little amphibole in the older, underlying sediments (75-100 mm). X-ray diffraction study of hundreds of river suspended sediment samples also indicates no detectable cummingtonite-grunerite (<1%) and only 1-2% amphibole in the natural sediments entering Western Lake Superior. Much or all of the trace amphibole is the common, non-asbestiform mineral hornblende.

Further indication of the recent addition of cummingtonite-grunerite to Western Lake Superior water is provided by x-ray diffraction patterns of many suspended sediment samples saved from the years 1940, 1950, and 1964 (Figure 2). All samples from 1940 and 1950 did not contain detectable amounts of cummingtonite-grunerite and little if any other amphibole minerals as indicated by a (110) peak at 10.6° 2θ (d = 8.34 Å). All of the 1964 samples, however, contained large concentrations of cummingtonite-grunerite as shown by the appearance of large (110) and (210) peaks. The (110)/(310) peak ratios for these samples are typical of those found for taconite tailings samples.

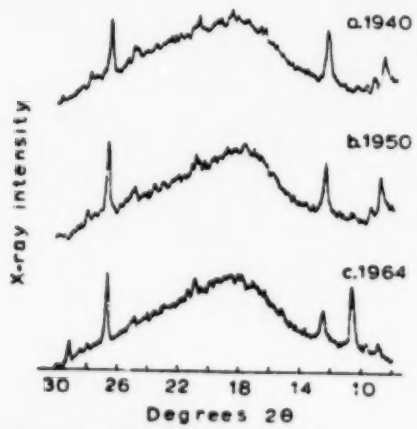

FIGURE 2---X-RAY DIFFRACTION PATTERNS FOR SUSPENDED SOLID SAMPLES OBTAINED FROM THE DULUTH MUNICIPAL WATER SUPPLY INTAKE: A HISTORICAL RECORD OF AMPHIBOLE CONCENTRATIONS IN DULUTH'S DRINKING WATER

In 1973, study of the morphology of amphibole particles in fine taconite tailings by transmission electron microscopy revealed the presence of many asbestiform fibers (Figure 3). The realization that many of these cummingtonite-grunerite fibers are indistinguishable from amosite asbestos fibers lead to concern over the use of Western Lake Superior water for municipal drinking water supplies. This concern was based on the association between human asbestos exposure and increased rates of cancer of the gastrointestinal tract and peritoneum (1) and daily x-ray diffraction analyses of Duluth, Minnesota drinking water samples which indicated the constant presence of high concentrations of taconite tailings. Transmission electron microscope analysis of Duluth water samples confirmed the presence of many amphibole fibers.

Since the discovery of asbestiform amphibole fibers in the water supplies of Silver Bay, Beaver Bay, Two Harbors, Duluth, and Cloquet, Minnesota, extensive sampling programs by the Environmental Protection Agency and other groups have been undertaken for electron microscope fiber counts. These analyses while in agreement with the x-ray diffraction results, are very expensive, time-consuming, and imprecise. At this time fiber counts done by different laboratories are not comparable and intralaboratory replicate results usually vary by ± 50% of the mean. The amphibole fiber concentrations generally correlate with the amphibole mass concentrations determined by x-ray diffraction. Thus x-ray diffraction monitoring of water samples combined with occasional electron microscope fiber counts offers a faster, less expensive, and probably more accurate measure of amphibole fiber contamination. This technique has been particularly useful for evaluating various filtration media's abilities to remove amphibole fibers from drinking water.

AMPHIBOLE ANALYSIS OF WATER SAMPLES

Water samples from Western Lake Superior public water supplies, normally ten liters in volume, are pressure filtered through 0.45μ membrane fibers. When the turbidity of the sample is known, the volume filtered is adjusted to give a 4-8 mg sediment sample. The total suspended solids are determined by difference and a weighing correction applied to compensate for a small filter weight loss due to leaching (2). Distilled water blanks are run periodically to check for contamination. The dry membrane filter with sample is fastened to a glass slide with a thin film of lacquer, the filter edges trimmed, and the slide directly examined with a Norelco vertical diffractometer (copper K_α radiation) with a graphite crystal focusing monochromator.

The amphibole fibers and cleavage fragments assume a preferred orientation such that the c-axis, which corresponds to the long dimension of the fiber, is parallel to the filter surface. This

FIGURE 3---ELECTRON MICROGRAPH OF <2μ TACONITE TAILINGS. a) LOW MAGNIFICATION (2,500X). b) HIGHER MAGNIFICATION (12,500X) VIEW OF AN AMPHIBOLE FIBER BUNDLE

causes the (110) reflection and, to a lesser extent, the (310) reflection intensities to be enhanced, permitting the detection of trace amounts of amphibole. As little as 0.05 mg of <2μ cummingtonite-grunerite produces measurable (110) and (310) peaks.

A semi-quantitative measurement of the amphibole concentration is made by an external standard technique. This technique has been

used to estimate trace amounts of chrysotile asbestos and amphibole asbestos in dust samples on membrane filters (3,4) and fulfills the need for rapid, standardized estimates of amphibole concentration in samples which are not amenable to the use of an internal standard. Three potentially large sources of systematic error had to be considered before accepting the external standard model: variability of particle size, sample mass absorption coefficient, and amphibole preferred orientation.

The external standard chosen for the preparation of standard curves of x-ray peak intensity versus mass of amphibole was the amphibole mixture found in the <2μ taconite tailings. This choice was made since the predominant amphibole in Western Lake Superior water is cummingtonite-grunerite from taconite tailings and natural amphibole concentrations in Lake Superior water are normally not detectable by x-ray diffraction. The <2μ taconite tailings were determined by the x-ray diffraction of cummingtonite-grunerite/quartz mixtures to contain approximately 80% amphibole and 20% quartz. Most of the amphibole is cummingtonite-grunerite with some actinolite-tremolite. Larger size fractions of the tailings contain less amphibole and more quartz with a small percentage of magnetite.

Reference samples were prepared by adding known amounts of the <2μ amphibole standard to ten liter samples of Lake Superior water having no detectable amphibole minerals. This water, obtained from Grand Marais, Minnesota, contained 0.4 mg/l suspended solids which consisted primarily of organic debris, diatoms, quartz, and clay minerals. These standard samples were then filtered and analyzed by x-ray diffraction in the same manner as unknown samples. The resulting x-ray diffraction patterns are identical in appearance to those for Duluth water samples.

The <2μ amphibole particle size (by gravity settling) for the external standard was shown to be appropriate by a centrifugation size-separation of Duluth water suspended solids from samples taken on fifteen different days. Ninety-five percent of the suspended solids were in the <2μ fraction with only a small amount of amphibole in the 5% which was >2μ. Thus variability in diffracted x-ray intensity due to mineral particle size >2μ is insignificant.

The filtration of ten liters of Duluth water normally results in 4-8 mg of suspended solids retained on the 0.45μ membrane filter. When the suspended solids exceed 0.8 mg/l, smaller volumes are filtered. A sample weight of 8 mg and an average density of 2 g/cm^3 results in a hypothetical sample thickness of 3μ on the filter. This thin sample thickness should preclude variability due to differences in sample absorption coefficients. Direct evidence for this is provided by the linearity of a plot of percent amphibole versus x-ray intensity for samples in this weight range; the uniform

intensity of filter background in the x-ray diffraction pattern with increasing sample weight to 10 mg; and the linearity of a plot of quartz peak (d = 3.33 Å) intensity versus weight of quartz, regardless of total sample weight in the range 0–12 mg.

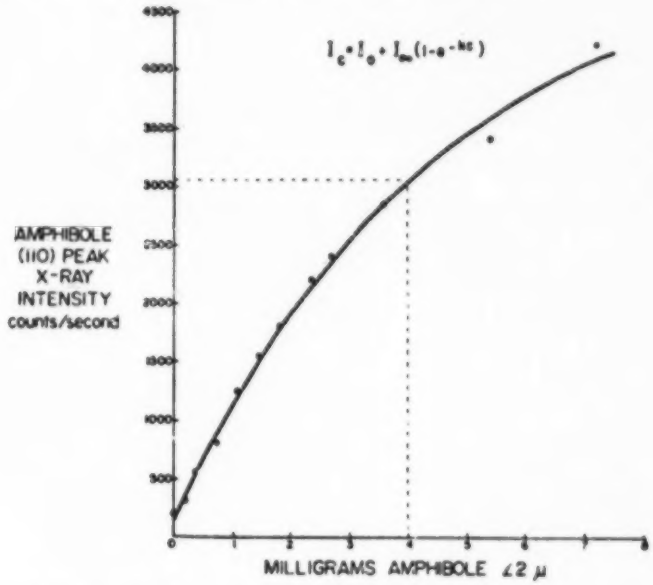

FIGURE 4—EXTERNAL STANDARD CURVE FOR AMPHIBOLE SEMI-QUANTITATIVE ANALYSIS

The non-linearity of the external standard curve (Figure 4) is due to a decreasing degree of preferred orientation as the amount of amphibole increases. This is indicated by decreasing amphibole (110)/(310) and amphibole (110)/quartz peak ratios with increasing weight of the standard amphibole-quartz mixture on the filter. The utility of the external standard curve depends on how well the curve models amphibole preferred orientation in environmental samples. Similar curves based on samples prepared with increased amounts of natural sediment agreed well with the standard curve used. With large amounts of natural sediment, the amphibole peak intensity is weakened which would cause an underestimation of amphibole concentrations. Other standard curves were employed to estimate the amphibole concentration in the few samples with a very high concentration of non-amphibole minerals.

External standard curves, such as Figure 4 were plotted from the non-linear least squares refinement of amphibole mass versus amphibole (110) peak intensity data points. The data fit an equation of the form: $I_C = I_o + I_\infty(1 - \exp{-kC})$, where I_C = intensity at concentration C (mg amphibole); I_o = intensity at C = 0; I_∞ = intensity at C = ∞; and k is a constant. This equation is consistent with a model in which the degree of preferred orientation decreases as more amphibole particles are placed on the membrane filter. Standard curves utilizing amphibole (110) peak height above background are identical to curves plotted from the (110) peak areas. Both measurements are used and give the same amphibole concentrations for environmental samples. Use of an amphibole (310) peak curve gives the same results but with less precision due to lower peak intensity.

Replicate (five) analyses of Duluth water samples indicate a standard deviation of ± 3% for determining amphibole concentrations in typical samples with 0.1-0.3 mg/l amphibole. For samples having lower amphibole concentrations (<0.1 mg/l) and high suspended solids (>1.0 mg/l), this precision is reduced to ± 25%. Overall suspended solids determinations have a standard deviation of ± 6% of the mean. Detection limits for determining amphibole concentration depend on the volume of water filtered and can be as low as 0.5 µg/l.

WATER SUPPLY AMPHIBOLE ANALYSIS

Daily analyses of Duluth water samples for amphibole and suspended solids concentrations began in March 1973 and continues to date. Results through January of 1974 are shown in Figure 5 with climatological data and intake water temperatures. X-ray diffraction analysis provides a picture of daily and seasonal fluctuations in amphibole and suspended solids concentrations. For example, periods of heavy rainfall are followed by abrupt increases in suspended solids due to river run-off and shore erosion. These increases in suspended solids do not coincide with increases in amphibole, indicating a different source for amphibole sediment.

Maximum amphibole concentrations (up to 0.8 mg/l) occur in the late fall and spring. Minimum amphibole concentrations (0.04 mg/l) occur during the late summer and early fall when a thermocline is present in Western Lake Superior. The average amphibole concentration measured was 0.19 milligrams per liter with 0.83 milligrams per liter total suspended solids.

During the period August 22-November 28, 1973, personnel from Region V of the Environmental Protection Agency obtained weekly water samples from municipal water supplies using Lake Superior water from Grand Marais, Minnesota to Marquette, Michigan. These

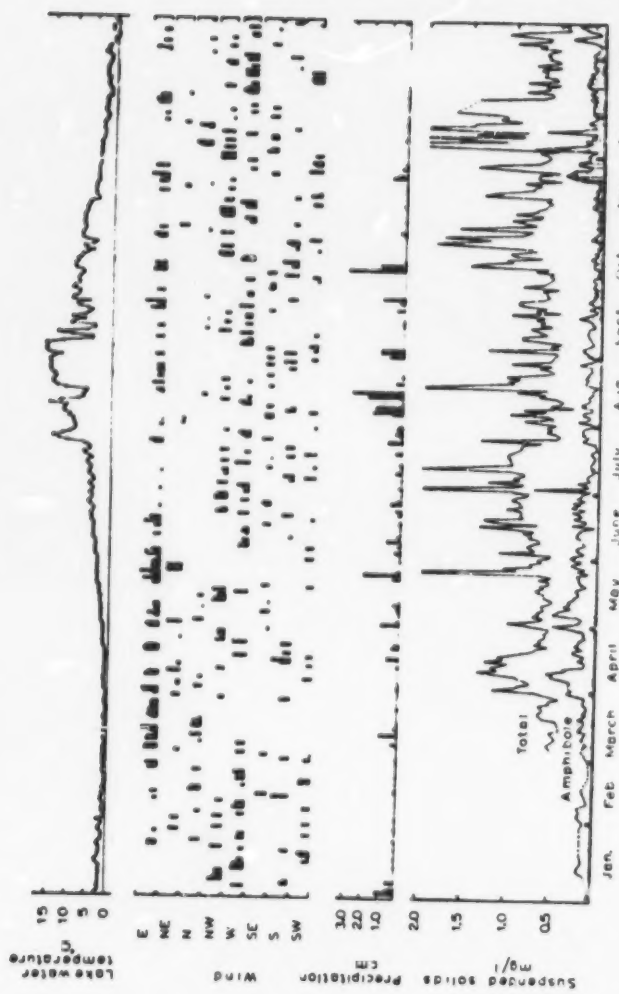

FIGURE 5---DAILY AMPHIBOLE AND SUSPENDED SOLIDS CONCENTRATIONS FOR DULUTH WATER WITH CLIMATOLOGICAL DATA AND WATER INTAKE TEMPERATURES

samples were analyzed for amphibole mass concentration at the National Water Quality Laboratory and amphibole fiber concentration by transmission electron microscopy at the Ontario Research Foundation in Sheridan Park, Ontario and McCrone Associates in Chicago, Illinois. Figure 6 depicts the average x-ray diffraction and electron microscope measurements for each station. The agreement between these two measurements is obviously very good. The pattern of maximum concentrations at Beaver Bay and decreasing concentrations in a counterclockwise direction around Western Lake Superior is consistent with large quantities of amphibole fiber discharged at a point between the Silver Bay and Beaver Bay, Minnesota water supply intakes and then transported towards Duluth (southwest) by the predominantly counterclockwise currents of Western Lake Superior (5).

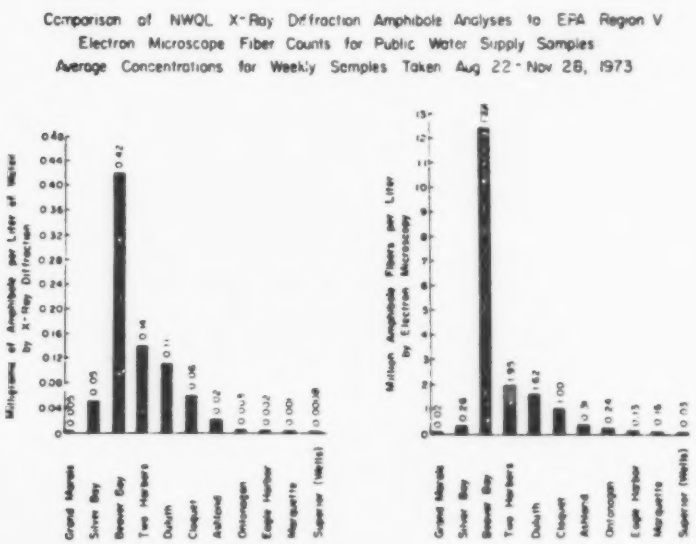
Comparison of NWQL X-Ray Diffraction Amphibole Analyses to EPA Region V
Electron Microscope Fiber Counts for Public Water Supply Samples
Average Concentrations for Weekly Samples Taken Aug 22 - Nov 28, 1973
Milligrams of Amphibole per Liter of Water by X-Ray Diffraction
Million Amphibole Fibers per Liter by Electron Microscopy
Grand Marais
Silver Bay
Beaver Bay
Two Harbors
Duluth
Cloquet
Ashland
Ontonagon
Eagle Harbor
Marquette
Superior (Wells)

FIGURE 6---COMPARISON OF AMPHIBOLE MASS CONCENTRATION DETERMINED BY X-RAY DIFFRACTION TO TRANSMISSION ELECTRON MICROSCOPE AMPHIBOLE FIBER COUNTS FOR LAKE SUPERIOR WATER INTAKES

ACKNOWLEDGEMENTS

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REFERENCES

1. I. J. Selikoff, E. C. Hammond and J. Churg, "Carcinogenicity of Amosite Asbestos," Arch. Environ. Health 25, 183-186 (1972).

2. J. G. Eaton and G. E. Likens, "Use of Membrane Filters in Gravimetric Analyses of Particulate Matter in Natural Waters," Water Resources Res. 5, 1151-1156 (1969).

3. A. L. Rickards, "Estimation of Trace Amounts of Chrysotile Asbestos by X-Ray Diffraction," Anal. Chem. 44, 1872-1873 (1972).

4. J. V. Crable, "Quantitative Determination of Chrysotile, Amosite, and Crocidolite by X-Ray Diffraction," Am. Ind. Hyg. Assoc. J. 27, 293-298 (1966).

5. C. E. Adams, "Summer Circulation in Western Lake Superior," Proc. 13th Conf. on Great Lakes Res., 862-879 (1970).

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SCIENCE

Asbestiform Amphibole Minerals: Detection and Measurement of High Concentrations in Municipal Water Supplies

Philip M. Cook, Gary E. Glass and James H. Tucker

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Asbestiform Amphibole Minerals: Detection and Measurement of High Concentrations in Municipal Water Supplies

Abstract. *Asbestiform amphibole minerals, which have been demonstrated to be associated with human health problems, have been detected in substantial quantities in municipal water supplies taken from western Lake Superior water. The total concentration of amphibole minerals in the Duluth, Minnesota, water supply, as measured by x-ray diffraction for daily samples of suspended solids, averages 0.19 milligram per liter with large fluctuations due to seasonal and climatological effects on lake circulation. Electron microscopic examination of these water samples confirms the presence of asbestiform amphibole fibers. A conservative estimate of the fiber count for 1973 Duluth water supply samples is 11 to 30 × 10⁶ amphibole fibers identifiable by electron diffraction per liter of water with a mass concentration of 1 to 30 micrograms per liter.*

The inhalation of asbestos fibers has long been recognized as a serious occupational and environmental health problem. Moreover, excessive rates of gastrointestinal and peritoneal cancer are associated with occupational exposure to asbestos (*1*). Recently it has been suggested that the ingestion of asbestiform minerals causes an increased incidence of gastrointestinal cancers (*2*). The presence of asbestiform particles in parenteral drugs (*3*), beverages (*4*, *5*), food (*6*), and drinking water (*5*, *7*) has been reported, and the migration of these fibers through the rat bowel wall has been demonstrated by several workers (*8*). The rapid transport of large intact starch granules and other particles throughout the human body after ingestion has also been reported (*9*).

Although natural sources of asbestiform minerals are known to contribute to fiber concentrations in drinking water, particularly in areas of serpentine rock, industrial discharge and mining operations can also produce high concentrations of asbestiform minerals in drinking water supplies (*7*). The contribution to water supplies from asbestos-cement pipe is now being studied by the Environmental Protection Agency.

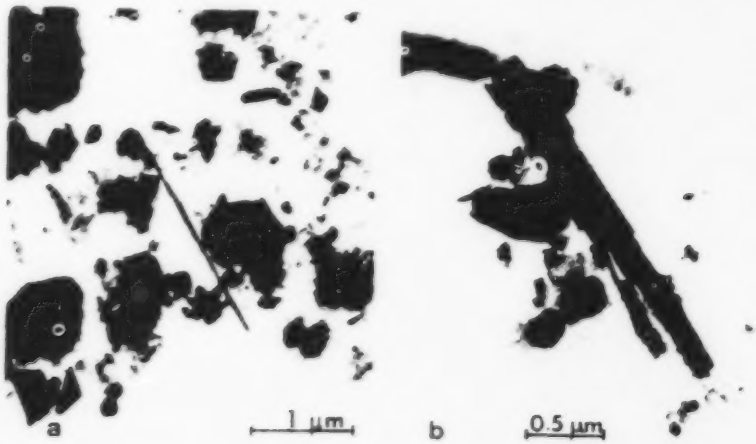

Fig. 1. Electron micrographs of amphibole fibers filtered from Duluth drinking water: (a) fiber approximately 2.2 μm long and 0.04 μm wide; (b) fiber approximately 2.9 μm long which is a bundle of many individual fibrils. Amphibole fibers are present with other minerals, diatoms, and organic detritus; thus it is difficult to identify all the amphibole fibers present.

Such contamination is invariably due to chrysotile asbestos, since approximately 95 percent of the asbestos fiber used in North America is chrysotile (*10*). Other asbestos minerals, all of which are in the amphibole group of hydrated silicates, include amosite, crocidolite, anthophyllite, tremolite, and actinolite.

We report here the discovery of asbestiform amphibole fibers in public water supplies taken from western Lake Superior water. We have studied the variations in the concentration of asbestiform minerals in this water over the past year by x-ray diffraction and electron microscopic techniques. The predominant amphibole present is cummingtonite-grunerite, which is represented by the formula $(Mg,Fe)_7Si_8O_{22}(OH)_2$. The asbestiform cummingtonite-grunerite of commercial importance is amosite. In addition, smaller amounts of tremolite-actinolite and hornblende are found in the amphibole fraction of suspended solids filtered from western Lake Superior water. The concentration of amphibole (*11*), particularly cummingtonite-grunerite, was found to be below detection limits (< 0.02 mg/liter) at Thunder Bay, Ontario, and Grand Marais, Minnesota; detectable at Silver Bay, Minnesota; high (> 0.1 mg/liter) at Beaver Bay, Two Harbors, and Duluth, Minnesota; and detectable in Cloquet, Minnesota, water which is also used by Superior, Wisconsin.

Examination of samples of suspended solids from the Duluth water supply by transmission electron microscope reveals the presence of diatom fragments, organic debris, quartz particles, some clay minerals, and amphibole particles ranging from blocky cleavage fragments to asbestiform fibers (Fig. 1). High-magnification electron micrographs (Fig. 1b) show that many fibers consist of smaller fibers, or fibrils, held together in bundles. The bundle nature, the fuzziness observed owing to the presence of fibrils within the fiber, and the ragged ends of the fibers have all been listed as criteria for the morphological identification of asbestos fibers by transmission electron microscopy (*12*).

Although amphibole fibers as long as 20 μm have been observed in Duluth

water samples, most are less than 5 μm long with many less than 1 μm long. There has been considerable debate (*13*) over the carcinogenicity of inhaled asbestos fibers smaller than 5 μm, although occupational and environmental exposure to asbestos which results in cancer invariably involves more fibers smaller than 5 μm than fibers larger than 5 μm. Less is known of the significance of fiber length when the fibers are ingested.

Amphibole fiber counts by electron microscopy (*14*) showed millions of amphibole fibers per liter in samples of Duluth water. The amphibole-like fibers may be positively identified by their selected-area electron diffraction patterns (SAED). For reasons of size, orientation, or particulate interference many amphibole fibers do not provide diagnostic diffraction patterns, and thus not all the fibers present were counted. The presence of some chrysotile fibers was also noted.

A comparison of the analysis of the water samples by x-ray diffraction and electron microscopy permits the estimation of fiber counts for other Duluth water samples. The comparison rests on the assumption that the mass of total amphibole present is related to the number of amphibole fibers. This requires a constant particle size distribution for the samples compared, as was observed for the Duluth water samples. We estimate a range of (1 to 30) $\times 10^6$ SAED identified amphibole fibers per liter of water with a mass concentration of 1 to 30 μg/liter. The concentration of fibers in the drinking water varies with lake conditions and tends to decrease with the increasing residence time of the water in the distribution system. Occasional peak concentrations (up to 10^9 fibers per liter) can result from the resuspension of settled sediment in the water lines. These amphibole asbestiform fiber counts and particularly mass concentrations are much higher than the values reported for chrysotile fiber contamination in 22 municipal water supplies in the Province of Ontario (*7*). At Thunder Bay, which, like Duluth, uses unfiltered Lake Superior water, 0.8×10^6 chrysotile fibers per liter with a mass concentration of 0.0002 μg/liter were found.

The daily variations in the amphibole concentrations of Duluth water supply samples, as calculated from the amphibole x-ray diffraction peaks (*11*), are depicted in Fig. 2. During 1973, the amphibole concentrations varied from 0.03 to 0.80 mg/liter with a mean concentration of 0.19 mg/liter. The mean percent (by weight) of the suspended solids identified as amphibole was 23 percent.

The effect of climatological conditions on the amount and mineralogical nature of the suspended solids in the Duluth water supply is most evident when heavy rainfalls are followed by an increase in the amount of suspended solids resulting from river runoff and shore erosion. On 24 May, for example, 4.1 cm of rainfall was recorded; this was followed by a brief period, beginning on 26 May, characterized by high concentrations of suspended solids in the Duluth water supply. The lag time represents the time needed for the river runoff to move downshore to the water intake. These storm-caused high concentrations of suspended solids have low percentages of amphibole; this finding was expected, since our study shows that suspended river sediments entering Lake Superior contain only 0 to 3 percent amphibole, mainly hornblende. The prevailing water circulation in western Lake Superior is known to be counterclockwise (*15*), consistent with the pattern of progressively increasing amphibole concentration which we find in lake water to the northeast of Duluth. The Duluth water intake, located at a depth of 20 m, may receive water with increased amphibole concentration when the surface water circulation from the northeast is promoted by extended periods of easterly and northeasterly winds, as during the periods of 29 March to 9 April, 29 April to 1 May, and 1 to 7 May. These same winds may also cause the resuspension of recently settled amphibole-rich sediment by wave action in the shallow water area around the water intake. A period characterized by very high concentrations of suspended solids (approximately 20 percent amphibole) occurred in December 1973 when strong easterly winds resuspended surface sediments and the river sediment input was low. Ice cover, which normally begins in January, prevents such wind-generated resuspension of lake sediment.

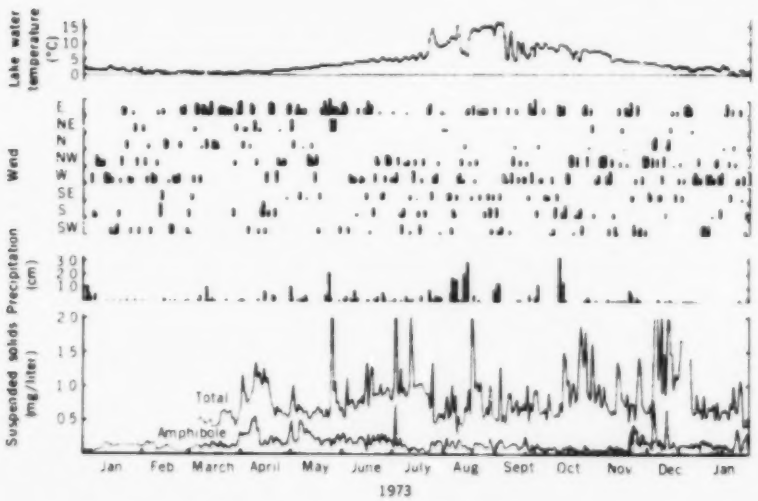

Fig. 2. Results of analyses (January 1973 through January 1974) of 10-liter Duluth, Minnesota, drinking water samples for amphibole and suspended solid concentrations. Daily sampling began on 19 March 1973. The dashed plot for prior dates indicates the period of less frequent sampling. Measurements of the concentrations of suspended solids were not made on samples taken before 6 March. Resultant wind direction and speed (wind scale, 0 to 30 km/hour) and precipitation data are the values as reported by the U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National Weather Service, for Duluth International Airport. Daily mean water temperatures are calculated from hourly Duluth water intake temperature data provided by the Duluth Water and Gas Department Lakewood pumping station. Climatological events which affect the amount and mineralogical nature of the suspended solids normally precede the observed change in water quality by 1 to 2 days.

Amphibole concentrations in Duluth water diminish during the period of increasing summer stratification of western Lake Superior water until fall overturn (the time period in Fig. 2 when water temperatures were greater than 4 °C), probably because of the decreased circulation of deeper lake water from the northeast. During times of isothermal conditions without ice cover this circulation is more pronounced, and thus the peak amphibole concentrations

occur in spring and late fall. Changes of water temperature at the intake during the months of summer stratification are often wind-related. Offstore winds (westerly or northwesterly) can cause upwelling which brings colder water to the intake such as on 6 and 11 September. Easterly or northeasterly winds during the months of stratification push warm surface water into the Duluth water intake area, causing higher water temperatures such as on 24 July.

A historical record of the types of amphibole minerals previously suspended in Lake Superior water may be derived from a study of the bottom sediments. Dell (*16*) reported hornblende as the predominant amphibole in the sand fraction of Lake Superior postglacial sediments with a trace of tremolite-actinolite also present in some cases. Our study (*17*) of the surficial sediments of western Lake Superior shows a clear pattern of a recently deposited sediment layer rich in cummingtonite-grunerite on top of older sediment which does not contain detectable amounts (< 1 percent) of cummingtonite-grunerite. This layer rich in cummingtonite-grunerite is thickest (90 m or more) and coarsest in the vicinity of a large taconite tailings discharge at Silver Bay, Minnesota (*18*). It spreads throughout much of western Lake Superior, becoming thin and diluted with other sediment at Duluth, which is at the western tip of the lake. Indication of recent changes in the mineralogy of suspended solids in western Lake Superior water is provided by our x-ray diffraction analysis of suspended sediment samples collected for several periods in the past by the City of Duluth water utility. Samples from 1939–1940 and 1949–1950 contain only trace amounts of amphibole with no detectable cummingtonite-grunerite, but all samples studied for the period 1964–1965 contained large amounts of amphibole (average, 31 percent of the total inorganic solids), most of which was cummingtonite-grunerite. The geological and limnological data indicate that the source of this large increase in amphibole material is the taconite tailings (*18*) that, since 1956, have been discharged into western Lake Superior at Silver Bay.

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References and Notes

1. E. E. Keal, *Lancet* **1960-II**, 1214 (1960); I. J. Selikoff, J. Churg, E. C. Hammond, *J. Am. Med. Assoc.* **188**, 142 (1964); P. E. Enterline and M. A. Kendrick, *Arch. Environ. Health* **15**, 181 (1967); I. J. Selikoff, E. C. Hammond, J. Churg, *J. Am. Med. Assoc.* **204**, 106 (1968); M. L. Newhouse and J. C. Wagner, *Br. J. Ind. Med.* **26**, 302 (1969).
2. Joint National Institute of Environmental Health Sciences–Environmental Protection Agency Conference on Biological Effects of Ingested Asbestos, Durham, North Carolina, 18–20 November 1973.
3. W. J. Nicholson, C. J. Maggiore, I. J. Selikoff, *Science* **177**, 171 (1972).
4. C. L. Berry, *Nature (Lond.)* **219**, 93 (1968).
5. H. M. Cunningham and R. D. Pontefract, *ibid.* **232**, 332 (1971).
6. R. B. Merlin, *Science* **173**, 1141 (1971); H. E. Bleier and R. J. Arion, *J. Occup. Med.* **15**, 92 (1973).
7. G. Kay, *Water Pollut. Control* **111**, 33 (1973).
8. G. E. Westlake, H. J. Spjut, M. N. Smith, *Lab. Invest.* **14**, 2029 (1965); R. D. Pontefract and H. M. Cunningham, *Nature (Lond.)* **243**, 352 (1973); H. M. Cunningham and R. D. Pontefract, *J. Assoc. Off. Anal. Chem.* **56**, 976 (1973).
9. G. Volkheimer and F. H. Schulz, *Qual. Plant. Mater. Veg.* **18**, 17 (1968); G. Schreiber, *Arch. Environ. Health* **29**, 39 (1974).
10. S. Spell and J. P. Leineweber, *Environ. Res.* **3**, 166 (1969).
11. By x-ray diffraction analysis of suspended solids filtered from 10-liter water samples, we made semiquantitative estimates of the amphibole concentration with the use of an external standard. This technique has been used to estimate trace amounts of chrysotile asbestos and amphibole asbestos in dust samples on membrane filters [A. L. Rickards, *Anal. Chem.* **44**, 1872 (1972); J. V. Crable, *Am. Ind. Hyg. Assoc. J.* **27**, 293 (1966)] and fulfills the need for rapid, standardized estimates of amphibole concentration in samples that are not amenable to the use of an internal standard.
12. P. Gross, R. T. P. deTreville, M. N. Haller, *Arch. Environ. Health* **20**, 571 (1970).
13. Doubts about the carcinogenicity of small fibers stem primarily from the absence of tumors in animals subjected to short fibers. A recent study [F. Post, F. Huth, K. H. Friedricks, *Zentralbl. Bakteriol. Parasitenkd. Infektionskr. Hyg. Abt. 1 Orig.* **155** (5/6), 463 (1972)], however, reported that rats intraperitoneally injected with chrysotile fibers incurred about a 40 percent incidence of tumors for two different tests with small fibers (95 percent less than 5 μm and 99 percent less than 3 μm).
14. The fiber counts were carried out by the Ontario Research Foundation (ORF), Sheridan Park, Ontario. A comparison with literature values is normally not possible since different preparation and counting methods are often used. Because ORF results have been reported for other water samples (*7*), these values can be compared with these results. The ORF fiber-counting technique consists of filtering the water sample with a 0.1-μm membrane filter, ashing the filter by maintaining it at 450°C for 3 hours, dispersing the ashed sample in 4 ml of distilled water, and centrifuging a 1-ml aliquot onto a carbon-coated electron microscope grid which is examined at × 25,000 magnification on a transmission electron microscope (Jeolco model JEM 100U) at 80 kv. The Environmental Protection Agency is currently developing a standard method for the counting of asbestos fibers in environmental samples.
15. C. E. Adams, *Proc. 13th Conf. Great Lakes Res.* (1970), p. 862.
16. C. I. Dell, "Late Quaternary Sedimentation in Lake Superior," thesis, University of Michigan (1971).
17. P. M. Cook, G. E. Glass, R. W. Andrew, in preparation; R. W. Andrew and G. E. Glass, in *Proceedings of a Conference on the Matter of Pollution of Lake Superior* (U.S. Department of Interior–Federal Water Quality Administration hearings, 2nd session, April 1970) (O-401-869, Government Printing Office, Washington, D.C., 1970), vol. 1, pp. 226–250.
18. Cummingtonite-grunerite is found almost exclusively in metamorphic rocks, usually in metamorphosed iron formations. The eastern Biwabik iron formation in northeastern Minnesota has been contact-metamorphosed by the Duluth gabbro. B. M. French [*Minn. Geol. Surv. Bull.* **48**, 1 (1968)] has described in detail the formation of cummingtonite-grunerite in the metamorphosed iron formation near the Duluth gabbro. This cummingtonite-grunerite in many cases is acicular to asbestiform in habit and varies from iron-rich grunerite to magnesium-rich cummingtonite. (The infrared spectrum of a sample of cummingtonite-grunerite from the taconite iron ore body is identical to that of amosite asbestos. The infrared interpretation technique described by R. G. Burns and R. G. J. Strens [*Science* **153**, 890 (1966)] for cummingtonite-grunerite indicates that both samples have an Fe/(Fe + Mg) atom ratio of 0.76.) The taconite iron ore body has been mined, and, after the extraction of magnetite, the amphibole-rich tailings have been discharged since 1956 into western Lake Superior at Silver Bay, Minnesota.

25 January 1974; revised 31 May 1974

APPENDIX G UNIVERSITY OF MINNESOTA AT DULUTH ELECTRON MICROSCOPE ANALYSIS RESULTS OF PILOT WATER TREATMENT UNITS - RAW WATER FROM DULUTH LAKEWOOD INTAKE.

Date of sample	Filter utilized	Run No.	f/l x 10^6 Raw sample	Finished sample	Per Cent Removal
6/13			33.25		
6/13	MM-1	36		0.53	98
6/13	MM-2	57		0.07	99
6/13	ERD-1	1		6.93	79
o/17			10.64		
6/17	MM-1	39		0.23	98
6/17	MM-2	61		0.41	96
6/17	BIF	31		7.59[a]	--
6/17	ERD-1	4		7.07[a]	66
6/24			6.03		
6/24	MM-1	44		0.92	85
6/24	MM-2	71		0.825	86
6/24	BIF	37		8.17[a]	--
6/24	ERD-2	22		1.85[a]	69
6/28			5.54		
6/28	MM-1	48		0.51	91
6/28	MM-2	76		0.53[b]	90
6/28	BIF	47		0.83	85
6/28	ERD-2	28		0.73	87
7/3			2.99		
7/3	MM-1	52		0.91	69
7/3	MM-2	78		0.16	95
7/3	BIF	51		1.96	34
7/3	ERD-2	32		1.22	59
7/19			266.0		
7/19	MM-1	67		0.66	--
7/19	MM-2	96		0.95	--
7/19	BIF	70		2.00	--
7/19	ERD-2	40		4.16	--
7/23			26.0		
7/23	MM-1	70		0.35	99
7/23	MM-2	99		0.23	99
7/23	BIF	72		4.41	83
7/23	ERD-2	41		2.04	92
7/25			60.5		
7/25	MM-1	72		0.46	99
7/25	MM-2	101		0.43	99
7/25	BIF	73		0.921	99
7/25	ERD-2	43		0.964	98
7/30			26.6		
7/30	MM-1	74		0.18	99
7/30	MM-2	105		0.10	99

APPENDIX G (CONTINUED).

Date of sample	Filter utilized	Run No.	f/l x 10^6 Raw sample	Finished sample	Per Cent Removal
7/30	BIF	77		1.01	96
7/30	ERD-2	45		0.87	99
7/31			106.6[b]		
7/31	MM-2	106		0.64[b]	99
8/1			30.0		
8/1	MM-1	76		0.72	98
8/1	MM-2	107		0.14	99
8/1	BIF	79		1.70	94
8/1	ERD-2	46		0.79	97
8/6			10.2		
8/6	MM-1	78		0.20	98
8/6	MM-2	109		0.19	98
8/6	BIF	82		0.42	96
8/6	ERD-2	48		2.00	80
8/8			15.1		
8/8	MM-1	80		0.45	97
8/8	MM-2	111		0.16	99
8/8	BIF	84		1.52	90
8/8	ERD-2	49		0.34	98
8/13			20.0		
8/13	MM-1	82		0.38	98
8/13	MM-2	113		0.37	98
8/13	BIF	88		0.59	97
8/13	ERD-2	51		0.51	97
8/15			8.98		
8/15	MM-1	84		0.55	94
8/15	MM-2	114		0.43	95
8/15	BIF	89		1.27	86
8/15	ERD-2	55		1.53	83
8/20			25.3		
8/20	MM-2	118		0.15	99
8/20	ERD-2	59		0.81	97
8/22			13.6		
8/21	MM-1	86		0.31	98
8/22	MM-1	86		0.49	96
8/22	MM-1	86		0.37	97
8/23			17.0		
8/23	MM-2	119		0.26	98
8/23	ERD-2	63		1.71	90
8/28			10.4		
8/28	MM-2	122		0.11	99
8/28	BIF	103		1.05	90
8/30			17.8		
8/30	MM-2	124		0.18	99
8/30	BIF	105		0.65	96
8/30	ERD-2	68		0.29	98

APPENDIX G (CONTINUED).

Date of sample	Filter utilized	Run No.	f/l x 10^6 Raw sample	f/l x 10^6 Finished sample	Per Cent Removal
9/4			30.3		
9/4	MM-2	126		0.33	99
9/4	BIF	108		0.96	97
9/4	ERD-2	70		0.70	98
9/6			13.6		
9/6	MM-2	128		0.17	99
9/6	BIF	111		0.36	97
9/6	ERD-2	72		0.26	98
9/9			15.4		
9/9	BIF	113		0.33	98
9/9	ERD-2	73		0.64	96
9/10			--		
9/10	MM-2	131		0.27	--
9/11			13.0		
9/11	MM-2	133		0.30	98
9/11	BIF	115		0.28	98
9/13			30.0		
9/13	MM-2	137		0.24	99
9/13	BIF	117		0.47	98
9/13	ERD-2	78		0.51	98
9/16			20.3		
9/16	MM-2	138		0.51	97
9/16	BIF	118		4.89	76
9/16	ERD-2	79		0.81	96
9/17			12.8		
9/17	MM-2	139		0.64	95
9/19			13.8		
9/19	MM-1	87		1.46	89
9/19	MM-2	140		0.33	98
9/19	BIF	120		0.76	94
9/20			19.1		
9/20	ERD-2	85		0.45	98

[a] Value may be in error due to DE present in sample
[b] Cloquet Pipeline water

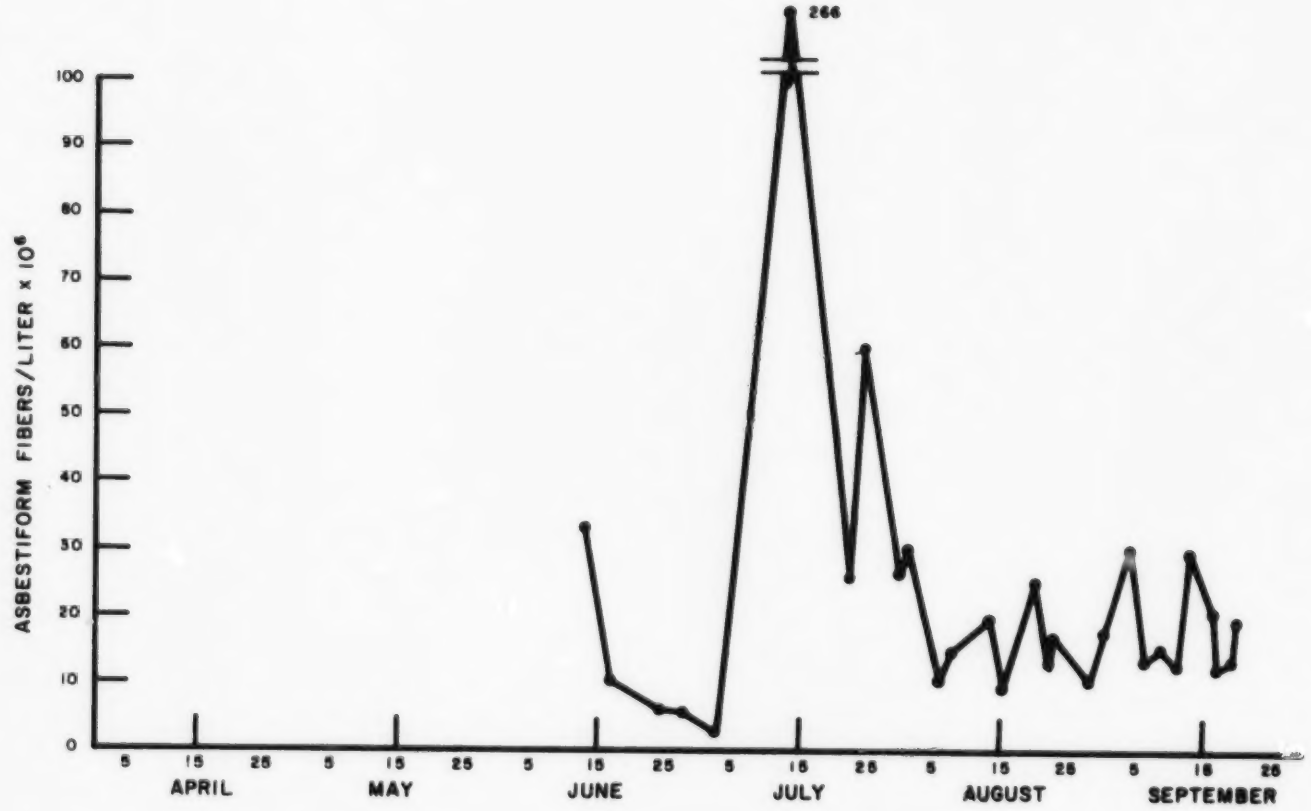

FIGURE 1. UNIVERSITY OF MINNESOTA AT DULUTH
ASBESTIFORM FIBER COUNTS
RAW WATER AT DULUTH LAKEWOOD INTAKE

UNIVERSITY OF MINNESOTA
DULUTH

School of Medicine
2205 East 5th Street
Duluth, Minnesota 55812

September 19, 1974

Mr. O. John Schmidt
Black & Veatch
Consulting Engineers
P. O. Box No. 8405
Kansas City, Missouri 64114

Dear Mr. Schmidt:

I am pleased to forward the following description of the methods by which we have been counting fibers here at the School of Medicine in Duluth.

Water samples were obtained from Black & Veatch Engineers at the Lakewood Pumping Station for the City of Duluth. The code information on each bottle was recorded and the bottles were then assigned random numbers in order to "blind" personnel involved in the subsequent steps of the analysis. The code was not broken until counting of all samples from a given week or weeks was completed.

Two-hundred milliliters of each sample were filtered through Nucleopore* filters with pore size of 0.2 microns. Particulate matter within the sample was collected on the dull surface side of the membrane filter, and a sediment faintly visible to the naked eye was observed with the majority of samples filtered. The filter was air dried and placed in a sealed plastic container until electron microscope grids were prepared.

At the time of grid preparation, each filter was cut in half with a fine scissors. One-half was returned to the plastic container for possible future use. The other half was inverted on two randomly placed copper electron microscope grids which had been placed on six layers of filter paper in a clean glass petri dish. The EM grids had been covered with a Formvar plastic film followed by a carbon coating. A single drop of chloroform was placed on the filter membrane over each grid position, fixing that portion of the membrane firmly to the surface of the coated grid. The filter paper in the petri dish was then saturated with chloroform to dissolve the remainder of the plastic filter, leaving the filtered particulate matter adhering to the coated surface of the grid.

Fibers were enumerated using a Philips Series 200 Electron Microscope at 10,000 X magnification. Any particle with nearly parallel sides, square ends, and an aspect ratio of 3 to 1 or greater was counted as a fiber. Electron diffraction was performed on a sufficient number of particles in each sample to ascertain that fibers of a given morphologic appearance had a crystalline diffraction pattern typical of chrysotile or amphibole asbestos.

Both of the grids prepared from a sample were studied. Particle enumeration continued until at least 25 fibers had been seen or until at least 20 grid squares along an equatorial plane had been studied. The total number of fibers seen in each grid square studied were recorded and averaged for the two grids from each filter. Appropriate mathematical factors were applied to convert particles seen into fibers per liter based upon the volume of water filtered and the cross-section area of the grid examined.

Agreement between the replicate samples averaged plus or minus 15 per cent and the analysis of the variance indicated that the correlation between the replicate samples was significantly greater than would have been expected by chance alone.

Sincerely yours,

R. E. Carter

Robert E. Carter, M.D.
Dean

REC:mk